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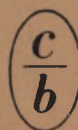
September, 1994

LITHOLOGY AND MINERAL RESOURCES

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A translation of *Litologiya i Poleznye Iskopaemye*

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**SULFIDE FORMATION IN THE REGION OF CONTEMPORARY PEAT
ACCUMULATION OF THE RIONI INTERMONTANE TROUGH.
COMMUNICATION 1. PATTERNS OF SULFIDE-FORMATION
PROCESSES IN PEAT BOGS OF THE COASTAL-
CONTINENTAL STRIP OF COLCHIS**

**P. P. Timofeev, L. I. Bogolyubova,
and L. Ya. Kizil'shtein**

UDC 553.31.661.2:553.97(479.22)

Data are given on the distribution of sulfate-reducing bacteria and sulfur in cross sections of peat deposits in the Colchian lowland, which is a region of contemporary peat accumulation in the Rioni intermontane trough. It was shown that the main source of sulfide sulfur in peat deposits is sulfate ions of seawater, and its accumulation in the sediments is controlled, on the whole, by genetic types and their position in the cross section in relation to the coastline. The closer to the shore and the deeper a particular genetic type of sediment lies, other conditions being equal, the greater the amount of sulfide sulfur that is present in peat bogs of the Rioni intermontane trough.

The conditions of sulfide mineralization in regions of contemporary and ancient peat accumulation have not been adequately studied. Meanwhile, such investigations are quite important in connection with the development of a general theory of the sedimentary process as a whole, including reconstruction of the geochemistry of ancient peat accumulation, and problems of sulfide mineral formation in particular. The authors set the task of studying sulfide formation in peat against the facial background of the sedimentary process, at the same time evaluating the whole set of landscape-geochemical, microbiological, and hydrochemical factors. The investigations were aimed at clarifying the essence of the process of sulfide formation as one of the most important processes of late syngensis and the early stage of lithogenesis, i.e., diagenesis. They also called for solution of general sedimentological problems, including questions of the genesis of sulfides in coal seams.

The work was conducted on the basis of data from peat bogs of the Abkhaz-Megrel, Poti, and Kobuleti basins,* which are regions of contemporary peat accumulation of the Colchian lowland entering into the composition of the Rioni intermontane trough. In most cases, contemporary peat bogs (Fig. 1), located on the Black Sea coast of the Colchian lowland, are separated from it by a beach ridge composed of marine sands. The width of the ridge in different sections of the coast varies from several tens of meters up to 800 m, and its height reaches 3-4 m, in places 6 m. The mouths of large and small rivers flowing into the sea cut through the beach ridge (from north to south, the Galizga, Okumi, Inguri, Tikora, Churia, Khobi, Rioni, Supsa, Natanebi, Choloki, Kintrishi, and others). Between the rivers are individual peat deposits in the form of large lenses. In some areas of the coast (Ochamchiri etc.), the upper parts of the peat bogs are eroding, and the lower parts are submerged directly under the water of the Black Sea [6, 19]. The material for the investigation was the complete cross sections of peat beds in all of the deposits of the Rioni intermontane trough, the composition of which includes genetic types of sediments of the bog, lacustrine-bog, lacustrine, alluvial, and coastal-marine facies.

* We drilled about 600 boreholes with a manual auger, together with Georgian geological organizations. Moreover, we described over 100 boreholes more than 25 m deep, which also were drilled by Georgian geological organizations. The map only shows boreholes used in the present article.

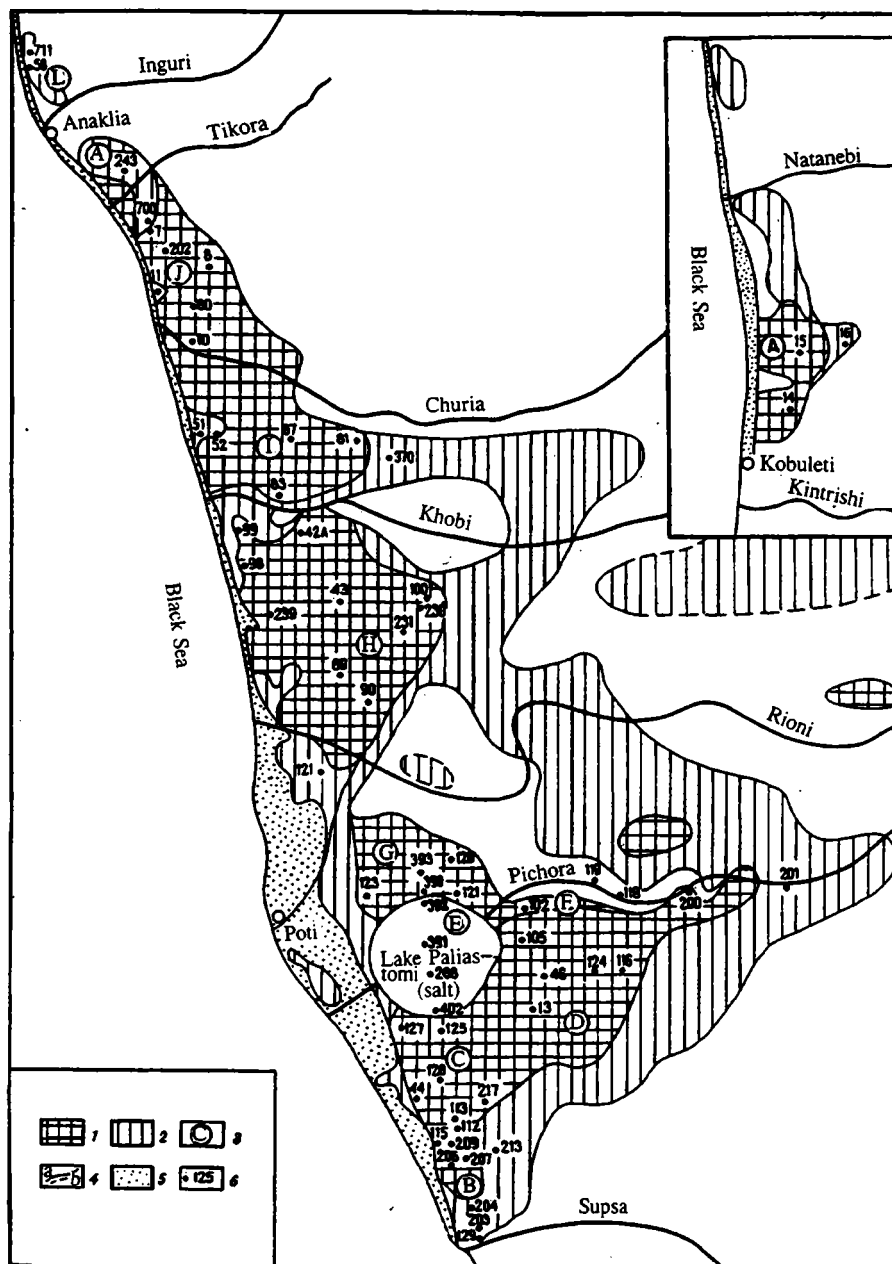


Fig. 1. Schematic map of location of peat bogs (deposits) and studied cross sections of manually drilled boreholes in the Colchian lowland. 1, 2) Depth of occurrence of peat bogs (1 - emerging to ground surface, 2 - covered by younger, terrigenous-clay sediments and buried to a depth of 25 m); 3) peat deposits: A) Kobuleti, B) Grigoleti, C) Moltakva, D) Imnat, E) Paliastomi, F) Pichora, G) Poti, H) Nabad, I) Churia, J) Anaklia, K) Tikora, L) Zorgat; 4) contours of peat bogs' extent (a - established, b - supposed); 5) beach ridge; 6) boreholes and their numbers.

MATERIAL COMPOSITION OF GENETIC TYPES OF SEDIMENTS IN PEAT BOGS OF THE COLCHIAN LOWLAND

The present article does not give detailed characteristics of genetic and facial types of sediments and their material composition, since such information can be found in [4-9, 13, 19-24, 25-27]. Here, we first consider the ratio of sulfate-reducing and saprophytic bacteria, then the behavior and amount of sulfate ions in relation to individual layers of the peat

TABLE 1. Total Sulfur Content in Sediments of Peat Beds in Various Deposits of the Colchian Lowland

Number of borehole (in numerator) and number of specimen (in denominator)	Depth of occurrence, m	Genetic type of sediment	S _{tot} %
1	2	3	4
Tikora deposit			
$\frac{243}{1}$	0,05	Clay with lumpy structure, rootlets of woody plants, and diatoms (soil)	0,50
$\frac{243}{2}$	0,10	Fine-grained silt with lumpy structure, rootlets of woody plants, atritus, and diatoms (soil)	0,92
$\frac{243}{3}$	0,55	The same with slightly lumpy structure	0,62
$\frac{243}{4}$	0,95	Fine-grained silt with woody stem remains, atritus, and leaves	1,20
$\frac{243}{5}$	2,20	Clay with lumpy structure, woody atritus, and plant rootlets	2,00
$\frac{243}{6}$	2,75	Clay with woody atritus, stem remains, leaves, and diatoms	2,37
$\frac{243}{7}$	3,10	Woody, gelinite-posttelinite, strongly clayey peat	0,45
$\frac{243}{8}$	3,25	Woody, gelinite-precollinite, slightly clayey	0,62
Anaklia deposit			
$\frac{11}{192}$	0,25	Fine-grained sand with rhizoid-sedge, gelinite-telinite peat	0,35
$\frac{11}{194}$	0,50	Sedge-reed, gelinite-precollinite, sandy peat*	1,54
$\frac{11}{196}$	1,50	Fine-grained sand with sedge-reed gelinite-precollinite peat	0,74
$\frac{11}{200}$	2,75	The same	0,93
$\frac{11}{202}$	3,25	Sedge-reed, gelinite-precollinite, strongly sandy peat	1,95
$\frac{11}{205}$	4,50	Rhizoid-sedge, gelinite-telinite, sandy peat with gelinite-precollinite	0,35
$\frac{11}{207}$	5,50	The same	1,68
$\frac{11}{208}$	5,75	"	0,91
$\frac{11}{212}$	6,50	Sedge-woody, gelinite-precollinite, strongly clayey peat	2,11
$\frac{8}{143}$	0,25	Woody, gelinite-precollinite, slightly clayey peat	0,57
$\frac{8}{144}$	0,50	The same	0,70
$\frac{8}{154}$	3,00	Woody, gelinite-precollinite, clayey peat	1,23
$\frac{10}{181}$	0,35	Woody, gelinite-precollinite, strongly clayey peat	2,62
$\frac{10}{182}$	0,66	Woody, gelinite-precollinite, slightly clayey peat	3,88
$\frac{80}{913}$	2,00	Sedge, gelinite-posttelinite, slightly clayey peat	1,93
$\frac{80}{163}$	2,50	Clay with sedge-woody, gelinite- precollinite peat	1,92
$\frac{80}{796}$	3,50	Sedge-reed, gelinite-precollinite, slightly clayey peat	2,43
$\frac{80}{912}$	5,50	Sedge, gelinite-posttelinite, slightly clayey peat	3,06
$\frac{80}{911}$	6,00	Woody, gelinite-precollinite, strongly clayey peat	2,63
Churia deposit			
$\frac{52}{752}$	1,50	Rhizoid-sedge, gelinite-telinite, strongly clayey peat with gelinite-precollinite	1,26
$\frac{52}{757}$	3,50	Fine-grained sand with woody, gelinite-posttelinite peat (strongly peaty)	5,65

TABLE 1. (continued)

Number of borehole (in numerator) and number of specimen (in denominator)	Depth of occurrence, m	Genetic type of sediment	S_{tot}^c %
1	2	3	4
<u>51</u> 740	1,50	Rhizoid-sedge, gelinite-telinite, slightly clayey peat with gelinite- precollinite	0,50
<u>51</u> 745	3,50	Sedge-reed, gelinite-precollinite, slightly clayey peat	1,25
<u>87</u> 377	0,75	Rhizoid-sedge, telinite-precollinite, slightly clayey peat with gelinite- precollinite	0,22
<u>87</u> 118	6,00	Reed, gelinite-precollinite, strongly clayey peat	0,78
<u>81</u> 863	3,00	Sedge-woody, gelinite-precollinite, clayey peat	0,15
<u>81</u> 628	4,50	The same	0,40
<u>81</u> 890	5,50	Woody, gelinite-precollinite, clayey peat	0,50
<u>83</u> 141	0,75	The same	0,27
<u>83</u> 839	4,25	Clay with sedge-reed, gelinite- precollinite peat (strongly peaty)	0,25
<u>83</u> 1166	5,25	Reed, gelinite-precollinite, strongly clayey peat	0,96
Nabad deposit			
<u>239</u> 1a	0,50	Rhizoid-sedge, gelinite-telinite peat with gelinite-precollinite	2,80
<u>239</u> 2	2,05	Sedge-reed, gelinite-precollinite, strongly clayey peat	3,02
<u>239</u> 3	3,55	The same, slightly clayey	3,50
<u>239</u> 4	4,55	The same, strongly clayey	3,00
<u>43</u> 645	1,50	Sedge-woody, gelinite-precollinite, slightly clayey peat	0,48
<u>43</u> 647	2,50	The same	0,32
<u>43</u> 650	4,00	Woody, gelinite-precollinite, strongly clayey peat	0,63
<u>43</u> 655	6,00	Sedge-reed, gelinite-precollinite, strongly clayey peat	0,93
<u>42a</u> 627	0,50	Woody, gelinite-precollinite, slightly clayey peat	0,29
<u>42a</u> 632	2,25	The same	0,32
<u>42a</u> 635	3,50	Clay with woody, gelinite-precollinite peat (strongly peaty)	0,79
<u>231</u> 5	5,50	Sedge-woody, gelinite-precollinite, clayey peat	0,21
<u>89</u> 486	0,50	Woody, gelinite-precollinite, clayey peat	0,24
<u>89</u> 947	1,50	The same, strongly clayey	3,17
Poti deposit			
<u>123</u> 216	6,50	Rhizoid-sedge, gelinite-telinite, clayey peat with gelinite-precollinite	0,80
Pichora deposit			
<u>121</u> 181	0,50	Sedge-reed, gelinite-precollinite, clayey peat	0,51
<u>121</u> 190	5,00	The same	0,40
<u>121</u> 191	5,50	Clay with sedge-reed, gelinite-precollinite peat (strongly peaty)	0,28
<u>120</u> 166	1,00	Sedge-reed, gelinite-precollinite, strongly clayey peat	0,40

TABLE 1 (continued)

Number of borehole (in numerator) and number of specimen (in denominator)	Depth of occur- rence, m	Genetic type of sediment	S _{tot} ^c %
1	2	3	4
<u>120</u> <u>170</u>	3.00	Sedge-reed, gelinite-precollinite, clayey peat	0.42
<u>120</u> <u>172</u>	4.00	Clay with woody, gelinite-posttelinite peat (strongly peaty)	0.46
<u>119</u> <u>147</u>	0.50	Sedge-reed, gelinite-precollinite, slightly clayey peat	0.55
<u>119</u> <u>152</u>	3.50	Sedge-reed, gelinite-precollinite, clayey peat	0.43
<u>119</u> <u>164</u>	9.50	Woody, gelinite-telinite, slightly clayey peat	0.70
Imnat deposit			
<u>13</u> <u>240</u>	1.00	Molinia-sphagnum, gelinite- telinite peat	0.11
<u>13</u> <u>242</u>	2.00	The same	0.08
<u>13</u> <u>244</u>	3.00	"	None
<u>46</u> <u>689</u>	1.55	"	0.24
<u>46</u> <u>691</u>	2.50	Rhizoid-sedge, gelinite-telinite peat with gelinite-precollinite	0.27
<u>46</u> <u>697</u>	5.50	The same	0.29
<u>46</u> <u>699</u>	6.50	Sedge-woody, gelinite-precollinite, slightly clayey peat	0.44
<u>124</u> <u>222</u>	0.50	Molinia-sedge-sphagnum, gelinite-telinite peat	None
<u>124</u> <u>227</u>	3.00	The same	0.27
<u>124</u> <u>228</u>	3.50	Rhizoid-sedge, gelinite-telinite peat with gelinite-precollinite	0.30
<u>124</u> <u>235</u>	7.00	Sedge-woody, gelinite- precollinite peat	0.49
<u>116</u> <u>119</u>	0.50	Rhizoid-sedge, gelinite-telinite, slightly clayey peat with gelinite-precollinite	0.30
<u>116</u> <u>121</u>	1.50	The same	0.26
<u>116</u> <u>123</u>	2.00	Clay with sedge-reed, gelinite-precollinite peat (strongly peaty)	0.18
<u>116</u> <u>124</u>	2.50	The same	0.25
<u>116</u> <u>127</u>	4.00	Sedge-reed, gelinite-precollinite, clayey peat	0.19
<u>116</u> <u>130</u>	5.50	Clay with woody, gelinite-precollinite peat (strongly peaty)	0.87
<u>116</u> <u>131</u>	6.00	Woody, gelinite-posttelinite, strongly clayey peat	0.94
<u>105</u> <u>69</u>	0.25	Sedge-reed, gelinite-precollinite, clayey peat	2.38
<u>105</u> <u>70</u>	1.00	The same	2.30
<u>105</u> <u>72</u>	2.25	"	2.40
<u>105</u> <u>73</u>	3.25	Reed, gelinite-precollinite, clayey peat	5.74
<u>105</u> <u>74</u>	4.75	Clay with sedge-reed, gelinite- precollinite peat (strongly peaty) and diatoms (soil)	4.67
<u>105</u> <u>75</u>	5.75	Clay with woody-reed, gelinite- precollinite peat (strongly peaty)	5.00
<u>105</u> <u>76</u>	6.50	Coarse-grained, carbonate silt	3.50

TABLE 1 (continued)

Number of borehole (in numerator) and number of specimen (in denominator)	Depth of occurrence, m	Genetic type of sediment	S ^c _{tot} , %
1	2	3	4
Moltakva deposit			
<u>127</u> <u>279</u>	0,50	Woody, gelinite-precollinite, clayey peat	1,02
<u>127</u> <u>281</u>	1,50	The same, gelinite-telinite	3,48
<u>44</u> <u>661</u>	2,00	Woody, gelinite-precollinite, slightly clayey peat	2,86
<u>44</u> <u>663</u>	2,50	The same, gelinite-posttelinite	2,91
<u>115</u> <u>109</u>	1,00	Woody, gelinite-precollinite, slightly clayey peat	0,96
<u>115</u> <u>113</u>	3,00	Fine-grained sand with sedge-reed, gelinite-precollinite peat (strongly peaty)	4,03
<u>115</u> <u>116</u>	5,00	Coarse-grained silt with woody attritus and stem remains	1,18
Grigoleti deposit			
<u>217</u> <u>1</u>	0,05	Woody, gelinite-precollinite, strongly clayey peat	0,34
<u>217</u> <u>2</u>	0,10	Clay with lumpy structure, rootlets, and woody attritus (soil)	0,42
<u>217</u> <u>4</u>	1,30	Clay with woody, gelinite-precollinite peat (strongly peaty)	2,20
<u>217</u> <u>5</u>	1,40	Woody, gelinite-precollinite, strongly clayey peat	0,14
<u>217</u> <u>6</u>	1,75	The same	0,30
<u>217</u> <u>9</u>	3,95	"	0,30
<u>209</u> <u>3</u>	1,80	Clay with woody, gelinite-precollinite peat (strongly clayey)	0,10
<u>209</u> <u>4</u>	2,30	Woody, gelinite-precollinite, slightly clayey peat	0,15
<u>209</u> <u>5</u>	3,75	Clay with lumpy structure and rootlets of woody plants (soil)	0,15
<u>209</u> <u>6</u>	4,25	Clay with woody attritus and leaves (slightly peaty)	0,16
<u>215</u> <u>4a</u>	2,00	Clay with woody attritus and stem remains of woody plants (slightly peaty)	0,07
<u>215</u> <u>5</u>	2,35	Clay with woody, gelinite-precollinite peat (peaty)	0,12
Kobuleti deposit			
<u>15</u> <u>267</u>	0,50	Sphagnum, gelinite-telinite peat	0,12
<u>15</u> <u>268</u>	1,00	The same	0,13
<u>15</u> <u>275</u>	3,50	Woody-sphagnum, gelinite- telinite peat	0,31
<u>14</u> <u>257</u>	0,50	Molinia-rhizoid-sedge, gelinite-telinite peat with gelinite-precollinite	0,17
<u>14</u> <u>258</u>	0,75	Reed, gelinite-precollinite peat with clay	0,43
<u>14</u> <u>259</u>	1,00	Clay with reed, gelinite-precollinite peat (strongly peaty)	0,22

* Sands are classified as fine-grained in all genetic types.

bogs' cross sections, components of the genetic types of peats and sandy-silty-clayey sediments,[†] and finally the genetic types of sediments as a whole. As shown below, this methodological approach is fundamentally significant, since it confirms the need for comprehensive study of the sedimentary process.

The genetic types of sediments (Table 1) of peat deposits in the Colchian lowland differ from each other in a set of traits, including the ratio of mineral and organic matter (OM), the botanical composition of peat-forming plants, and the degree of their biochemical decomposition. This set of traits characterizes their facial nature [6, 7, 19]. The degree of biochemical transformation of tissues of woody, herbaceous, and moss phytocenoses is manifested in telinite, posttelinite, precollinite, and collinite structures of organic matter dispersed in sediment, as well as concentrated in the form of peat beds. These structures of OM correspond to slight, relatively slight, relatively strong, and strong degrees of decomposition of the original plant material.

With respect to the ratio of organic and mineral[‡] matter, the sediments of peat deposits are subdivided into: peats (A^c up to 10%), slightly clayey peats (sandy or silty, A^c 10-25%), clayey peats (sandy or silty, A^c 25-35%), strongly clayey peats (sandy or silty, A^c 35-50%), clays, silts, or sands with 35-50% OM (strongly peaty), clays, silts, or sands with 25-35% OM (moderately peaty), clays, silts, or sands with 10-25% OM (slightly peaty), and clays, silts, or sands with less than 10% OM. In all of the genetic types, the sands are classified as fine-grained. With respect to botanical composition, the peat-forming plants belong to woody, herbaceous, and moss bog phytocenoses.

Among woody bog phytocenoses, alder is sharply predominant. Herbaceous ones are represented mostly by sedge and reed. Moss bog phytocenoses belong primarily to the sphagnum type. The genetic types of sediments are made up of plant associations homogeneous in their botanical composition (woody peats, clay with woody peat, sedge peats, reed peats, etc.), as well as mixed ones (woody-sedge peats, sedge-reed peats, clay with woody and herbaceous remains, etc.).

Contemporary peat accumulation in general, and in the Colchian lowland in particular, is characterized by a sharp predominance of gelation processes in the decomposition of plant material. Therefore, peats, as well as the organic matter of mineral sediments of the Abkhaz-Megrel, Poti, and Kobuleti basins of Colchis belong to the gelinite class. The names of the genetic types of peats and mineral sediments with dispersed organic matter include all of the traits listed above, reflecting which facies they belong to as a whole.

NATURE OF DISTRIBUTION OF SULFATE-REDUCING AND SAPROPHYTIC BACTERIA IN CROSS SECTIONS OF PEAT DEPOSITS

Study of the conditions of bacterial reduction of sulfates in sediments in regions of contemporary peat accumulation is limited to a small number of works [1, 2, 13], which does not correspond to the geological and geochemical role of these microorganisms that possess a unique ability to reduce sulfates to hydrogen sulfide at a normal temperature. Biogenic hydrogen sulfide interacts with iron ions, forming sulfides, the amount of which mainly determines the sulfur content of peats and then coals. Resolution of this question, together with detailed lithological and facial investigations, makes it possible to understand and explain the essence of biogenic synthesis of mineral matter in diagenesis, and also patterns of formation of the sulfur content of fossil coals.

Sediment samples for microbiological investigations were taken from the inner parts of the core of manually drilled boreholes and put into sterile test tubes, in the summertime. The conditions of development of sulfate-reducing bacteria in peat were clarified according to the procedure previously used to study peats in Lithuania [12]. In sediments from borehole 217 (see Fig. 1) of the Grigoleti deposit in Colchis, along with sulfate-reducing bacteria we also studied certain other groups of microorganisms that participate most actively in the process of microbiological decomposition of plant material during peat formation. They include saprophytic bacteria, actinomycetes, and fungi.

Test seedings of sulfate-reducing, as well as saprophytic bacteria were carried out and incubated in a temperature-controlled chamber at 28°C. Data from these tests were recorded at the end of 30 days. To reveal active saprophytic microflora, the times were reduced to 5 days. Incubation of peat samples for 30 days makes it possible to renew the activity

[†] Since peat is also a sediment, henceforth we will designate both of them as genetic types of sediment.

[‡] There is a significant difference between the content of mineral impurities in peat and ash content. In this case, ash content is used as an index of the content of the peat's mineral part.

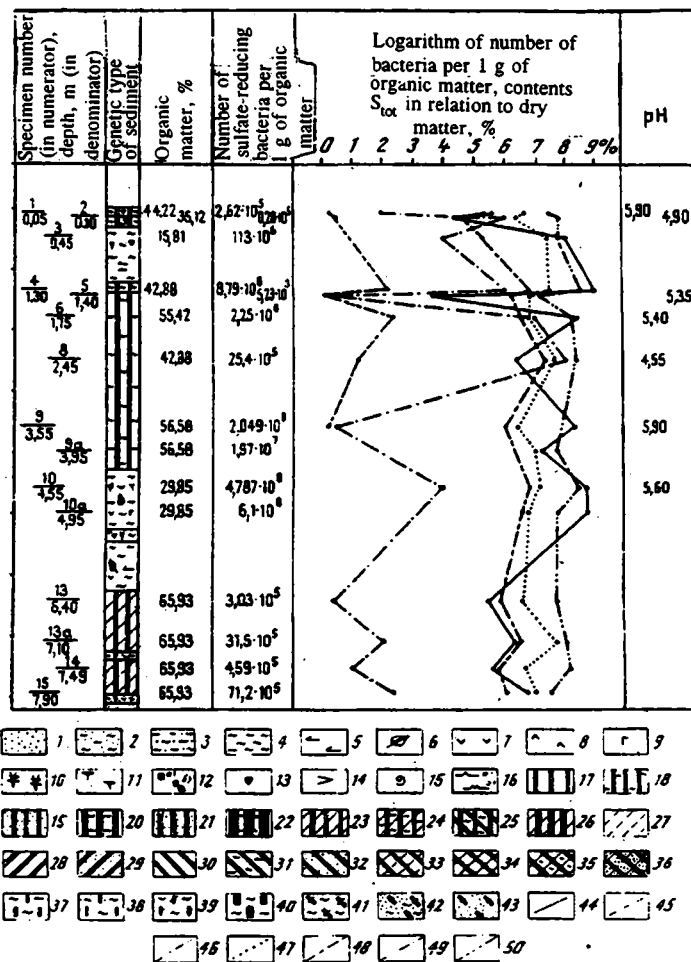


Fig. 2. Distribution of sulfate-reducing bacteria, pyrite, and total sulfur (borehole 217, Grigoleti peat deposit). Conventional notations for Figs. 2-13: 1) fine-grained sand; 2-3) silt (2 - coarse-grained, 3 - fine-grained); 4) clay; 5) stem remains; 6) leaf remains; 7-8) attritus (7 - woody, 8 - herbaceous); 9) gelated colloidal matter; 10) plant rootlets; 11) soil formations; 12) pyrite (a - a little, b - a lot); 13) iron hydroxides; 14) sponge spicules; 15) foraminifers; 16) diatoms (a - a few, b - a lot); 17) woody gelinite-precollinite peat; 18) the same, clayey; 19) the same, with sand; 20) woody, gelinite-posttelinite, clayey peat; 21) woody, gelinite-posttelinite peat with sand; 22) woody, gelinite-telinite, clayey peat; 23) woody-sedge, gelinite-precollinite peat; 24) woody-sedge, gelinite-precollinite, clayey peat; 25) woody-reed, gelinite-precollinite, clayey peat; 26) woody-sedge, gelinite-posttelinite peat; 27) rhizoid-sedge, gelinite-telinite, washed peat; 28) sedge, gelinite-precollinite peat; 29) the same with sand; 30) reed, gelinite-precollinite peat; 31) the same, clayey; 32) reed, gelinite-posttelinite peat with sand; 33) sedge-reed, gelinite-precollinite, washed peat; 34) sedge-reed, gelinite-precollinite peat; 35) the same, clayey; 36) sedge-reed, gelinite-precollinite peat with sand; 37) clay with woody, gelinite-precollinite peat; 38) fine-grained silt with woody, gelinite-precollinite peat; 39) clay with woody-sedge, gelinite-precollinite peat; 40) clay with woody, gelinite-posttelinite peat; 41) clay with sedge-reed, gelinite-precollinite peat; 42) coarse-grained silt with sedge-reed, gelinite-precollinite peat; 43) fine-grained sand with sedge-reed, gelinite-precollinite peat; 44) total number of sulfate-reducing bacteria (duration of test 30 days); 45) number of active sulfate-reducing bacteria (duration of test 5 days); 46) saprophytes; 47) actinomycetes; 48) fungi; 49) pyrite; 50) sulfur.

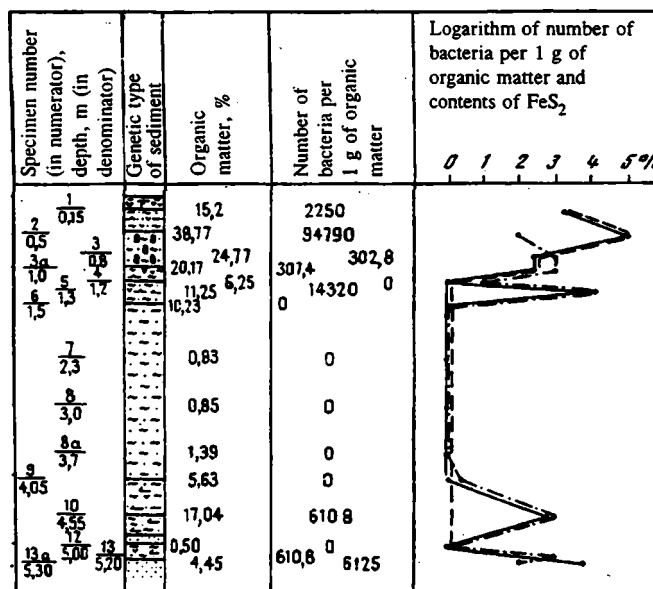


Fig. 3. Distribution of sulfate-reducing bacteria (duration of test 30 and 5 days) and pyrite through borehole 501 (Ochamchiri peat deposit).

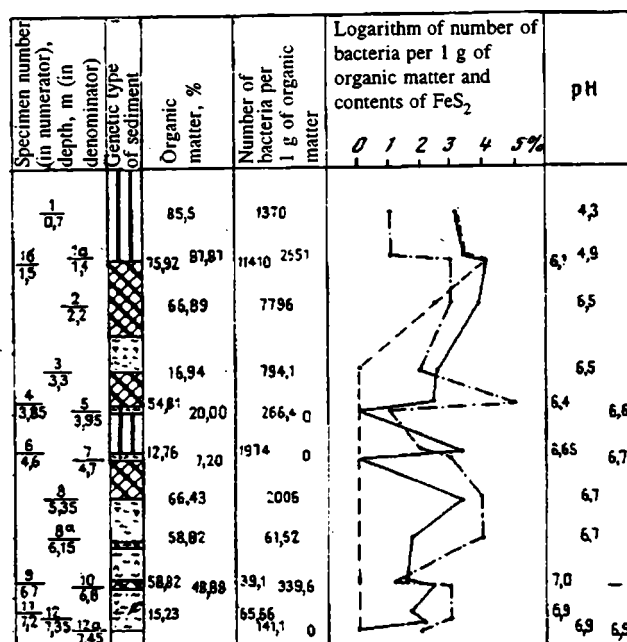


Fig. 4. Distribution of sulfate-reducing bacteria (duration of test 30 and 5 days) and pyrite through borehole 202 (Anaklia peat deposit).

of bacteria that are presently in a state of anabiosis in connection with submergence of the layers. This provides an opportunity to evaluate the number of bacteria in individual layers of peat through the cross section of a peat deposit throughout the whole time of its formation, which is in the range of 6000 years, according to data from absolute age determinations [7].

Joint analysis of the nature of distribution of sulfate-reducing and saprophytic microorganisms, which are responsible for decomposition of plant material in the peat-forming layer, in the cross sections of peat deposits shows a correlation between them. This fact is well illustrated by the curves in Fig. 2, where the maximum and minimum contents of the two

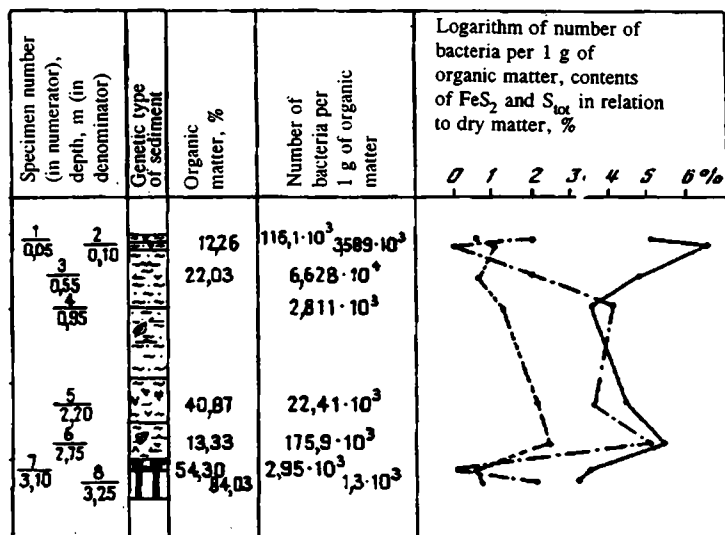


Fig. 5. Distribution of sulfate-reducing bacteria, pyrite, and total sulfur through borehole 243 (Tikora peat deposit).

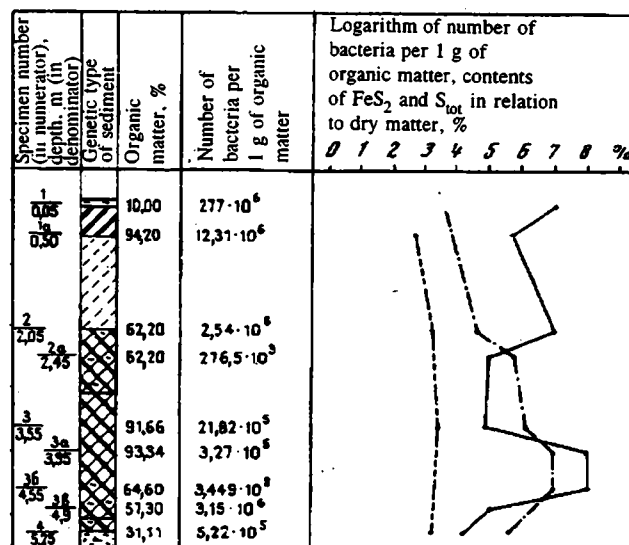


Fig. 6. Distribution of sulfate-reducing bacteria, pyrite, and total sulfur through borehole 239 (Nabad peat deposit).

coincide (with some exceptions) in individual layers of the peat deposit. At the same time, the first (upper) maximum of the number of saprophytes is above the first (upper) maximum of the number of sulfate-reducing bacteria. Consequently, manifestation of the greatest activity of sulfate-reducing bacteria is the next stage of development of the deposit's microorganisms following saprophytic microflora. In connection with this, the maxima and minima of saprophytic and sulfate-reducing bacteria in the cross section of a peat deposit, which are the same in amount on the whole, are not synchronous in time.

Coincidence of maximums of saprophytic and sulfate-reducing bacteria of the same amount indicates that saprophytic bacteria, by decomposing the complex matter of plant tissues in a peat-forming layer, convert it into simpler compounds that serve as readily assimilable food products for sulfate-reducing bacteria in the process of their vital activity [13]. In connection with this, the disappearance of saprophytic bacteria with depth [14] leads to the disappearance of active sulfate-reducing bacteria, as can be seen from consideration of the examples given for cross sections of peat deposits (Fig. 3, borehole 501; Fig. 4, borehole 202).

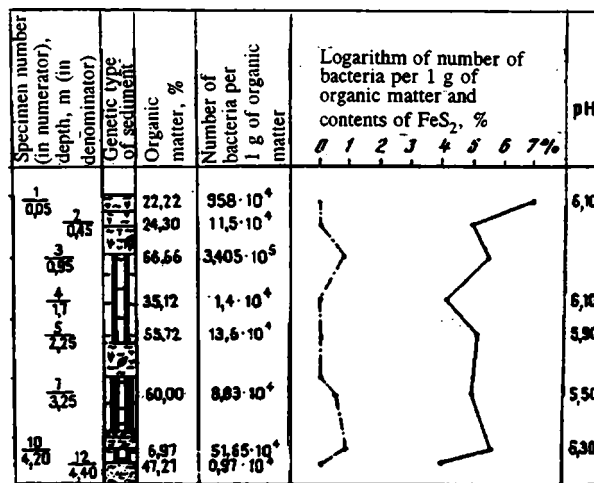


Fig. 7. Distribution of sulfate-reducing bacteria and pyrite through borehole 238 (Nabad peat deposit).

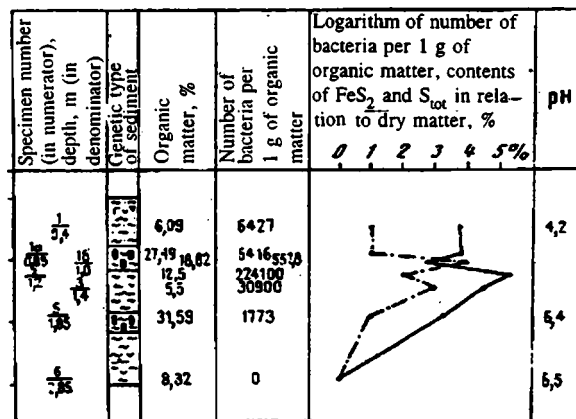


Fig. 8. Distribution of sulfate-reducing bacteria and pyrite through borehole 506 (Ochamchiri peat deposit).

At the same time, our attention is drawn to the depth of appearance of the upper (first) maximum of sulfate-reducing bacteria. From this point of view, test data obtained with incubation of sulfate-reducing bacteria for five days from sediments of borehole 501 (see Fig. 3) and 202 (see Fig. 4) are interesting. We can suppose that during this time only those bacterial cells that are in a vitally active state are activated. In analyzing the distribution of sulfate-reducing bacteria in sediments of the indicated borehole cross sections it was revealed that their maximum number is confined to clay sediments containing >15% organic matter, at a depth of 0.5 m (see Fig. 3) and in peat at a depth of 15 m (see Fig. 4). Further down through the cross section from these levels, the number of sulfate-reducing bacteria drops sharply in both boreholes. When the distribution curves for sulfate-reducing bacteria incubated for 5 and 30 days are compared, complete coincidence of the position of the first numerical maximums is found in both tests. This allows us to conclude that the first maximums of the number of sulfate-reducing bacteria in the upper parts of the deposits are manifested regardless of the length of the test, as a consequence of the fact that sulfate-reducing bacteria there are in an active state.

Analyzing the upper numerical maximums from this point of view for all of the investigated boreholes (see Figs. 2-4 and Figs. 5-11), we can easily discover their confinement to different depths of the deposits depending primarily on the genetic type of sediment and which facies and landscape it belongs to. In general terms, the maximum development of sulfate-reducing bacteria in clay sediments is connected with depths from 0.05 to 0.5 m, possibly as much as 1 m (see Figs. 2, 3, and 5-8), while in sediments represented by peats, the maximum number of sulfate-reducing bacteria is noted at depths from 1 to 1.5-1.8 m (see Figs. 4, and 9-11). Intensive development of sulfate-reducing bacteria in regions of contemporary peat accumulation is an indicator, as it were, of the degree of the medium's reduction [3, 18]. The beginning of the stage of

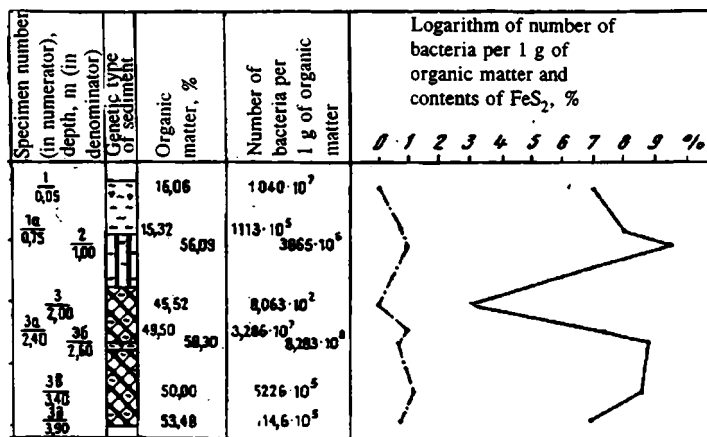


Fig. 9. Distribution of sulfate-reducing bacteria and pyrite through borehole 213 (Grigoleti peat deposit).

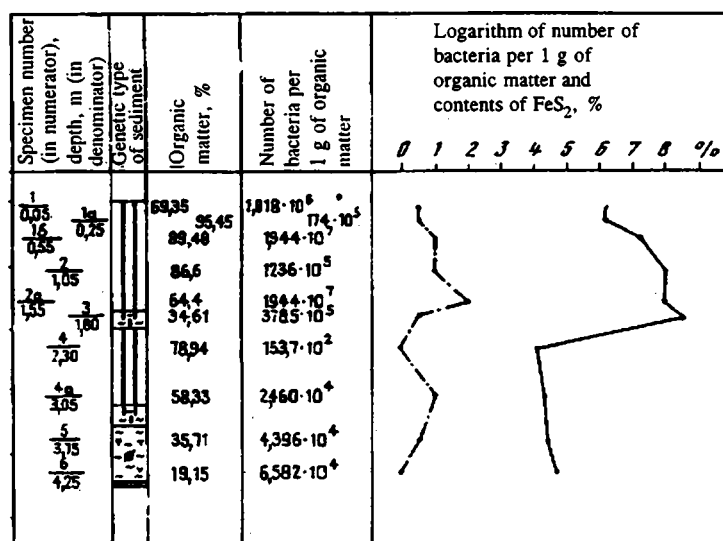


Fig. 10. Distribution of sulfate-reducing bacteria and pyrite through borehole 209 (Grigoleti peat deposit).

reduction changes of matter in diagenesis occurs at different times and at different rates in different genetic types of sediments. For clay sediments, as we can see from what has been set forth above, this stage already comes near the surface. For peats, it begins later and follows the stage of changes in dead plant material in conditions of the upper, aerated, so-called peat-forming layer. The thickness of the latter is determined by the level of the water table in the peat bog and varies in the range of 0.2-0.5 m, sometimes reaching 1 m [3, 10, 14].

We will consider the distribution of sulfate-reducing bacteria through the cross section of peat beds at various deposits. As we can see from the graphs (see Figs. 2-11), the distribution of sulfate-reducing bacteria in sediments of the peat beds' cross sections is uneven; the number of them varies in a wide range in one borehole, as well as when the boreholes are compared with each other. Contrasting layers are discovered with maximum and minimum contents of them, alternating in the peat beds' cross sections. Thus, in the cross section of borehole 202 of the Anaklia deposit (see Fig. 4), the maximum content of sulfate-reducing bacteria is noted at depths of 1.4, 4.7, 5.35, and 6.15 m. In borehole 243 of the Tikora deposit (see Fig. 5), the first maximum of the content of sulfate-reducing bacteria appears at a depth of 0.1 m. The beginning of appearance of the next maximum is found from a depth of 2.2 m. At the Nabad deposit, in borehole 239 (see Fig. 6) layers with maximum contents of bacteria are revealed at depths of 0.05, 2.05, and 3.95-4.55 m. In borehole 217 of the Grigoleti

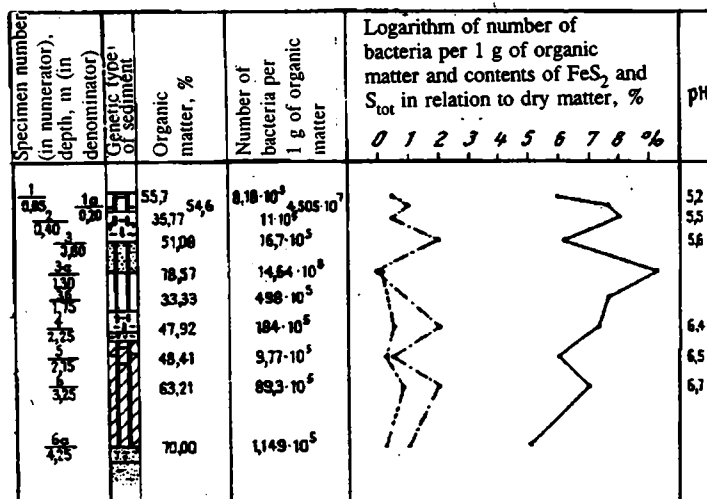


Fig. 11. Distribution of sulfate-reducing bacteria, pyrite, and total sulfur through borehole 208 (Grigoleti peat deposit).

deposit (see Fig. 2), the first maximum in bacteria content is at a depth of 0.45 m, then an increased number of bacteria is noted at depths of 1.4, 1.75, 3.95, and 4.55 m, etc. As we can see, the maximum development of sulfate-reducing bacteria is confined to different depths in different cross sections of peat beds. Thus, for example, in gelinite-precollinite, sedge-reed peats, with high or low ash content (see Fig. 6, borehole 239; Fig. 9, borehole 213), contrasting layers are noted with respect to the contents of sulfate-reducing bacteria. Different contents of sulfate-reducing bacteria are characteristic of clays displaying one or another amount of plant remains and attritus with a telinite or posttelinite structure. This is well illustrated by specimens 3, 5, 7, 10, etc. from borehole 202 (see Fig. 4), which are confined to certain depths. In a number of cases, approximately analogous amounts of sulfate-reducing bacteria are found in clays containing plant remains and in woody, gelinite-precollinite peats, as can be seen from comparison of the data for specimens 3, 10, and 10a, and 6 and 9 from borehole 217 (see Fig. 2). However, sulfate-reducing bacteria are not found in clay sediments that are almost sterile in relation to their content of organic matter. Thus, in borehole 501 (see Fig. 3), at depths of 1.5-4.05 m, in homogeneous silty blue clays without plant remains there are no bacteria, while clays located above and below this interval that do contain plant material decomposed to various degrees have a lot of sulfate-reducing bacteria. Analysis of the facts allows us to state that in eutrophic peat bogs of the Colchian lowland, other conditions being equal, the vital activity and development of sulfate-reducing bacteria requires a certain optimum of organic matter, which is the product of biogenic decay in the process of gelation of plant material of various botanical composition and has undergone some degree of decomposition. Since the development and vital activity of sulfate-reducing bacteria are linked with a wide range of genetic types of sediments in a lowland peat bog, their existence is not limited in this case by strict boundaries of the medium's pH, which vary, as the investigations showed, in the range of 4.2-5.6 and up to 7.0. As far as the development of sulfate-reducing bacteria in conditions of raised peat bogs of the sphagnum type, there are indications [13] of an unfavorable environment for their existence in the latter. This is explained by peculiarities of the chemical composition of sphagnum mosses' tissues [17], microbiological decomposition of which forms phenols, which have a suppressing action on the life of all microflora in the sphagnum type of peat.

If we pay attention to the number of sulfate-reducing bacteria in cross sections of peat beds as a whole and compare them with each other with respect to this trait, then it turns out that in the cross sections of peat beds of the Ochamchiri (see Figs. 3 and 8) and Anaklia (see Fig. 4) deposits the maximum number of bacteria does not rise above 4-5 (log of the number of bacteria per 1 g of organic matter). In cross sections of a peat bed in the Grigoleti deposit (see Figs. 2 and 9-11), there are almost twice as many sulfate-reducing bacteria, and the maximum number of them reaches a value of 9. At the Nabad peat deposit, in borehole 239 (see Fig. 6) the maximum bacteria content reaches a value somewhat more than 8, while in borehole 238 (see Fig. 7) of the same deposit their content decreases significantly. This phenomenon is explained by hydrochemical peculiarities of the region of peat accumulation and, in particular, by the concentration of sulfate ions in waters feeding the peat bog.

TABLE 2. Sulfur Content in Peat-Forming Plants of the Colchian Lowland

Type of peat-forming plant	Morphological parts of the plant	Ash content A ^c , %	Content of S _{tot} ^c , %	C _{org} , %
Reed	Plant as a whole	7.94	0.60	43.49
	Rhizome	11.38	1.08	42.13
	Leaves	7.55	0.52	44.42
	Stems	4.87	0.21	43.94
Sedge	Rootlets	2.27	0.10	46.42
	Vegetative organs	1.88	0.08	46.50
Alder	Root	4.41	0.19	45.75
	Trunk	1.97	0.07	48.05
Sphagnum	Plant as a whole	4.84	0.10	42.56
Rush	The same	1.85	0.07	46.94

Before we move on to consideration of the question of the source of sulfur in peat deposits as one of the components of sulfide mineral formation, we will analyze the contents of it in peat-forming plants.

CONTENTS AND DISTRIBUTION OF SULFUR IN SEDIMENTS OF PEAT DEPOSITS IN THE COLCHIAN LOWLAND

As the investigations showed, the total sulfur content in sediments of peat deposits in the Colchian lowland, like iron sulfides, varies in a wide range (from 0.1 to 5% and, in a number of cases, even more, calculated in relation to dry matter). To determine the source of sulfur in sediments of peat deposits of Colchis, we analyzed the ash of peat-forming plants growing in the bogs (Table 2).

As we can see from Table 2, the sulfur content is not the same in various plants; the greatest amount of it is noted in reed, which is due to its ecological peculiarities, characterized by relatively high mineralization of river, lake, and sea waters feeding the peat bogs. This also results in the plant's relatively high ash content. Comparison of the sulfur content of lowland peats of different botanical composition with that of peat-forming plants shows that there are differences between them to varying degrees. If the sulfur in reed (see Table 2) amounts to 0.6% of the plant as a whole, then in reed peats (see Table 1) the amount of it can increase by as much as 10 times, with the exception of isolated cases when the values are close. The sulfur content in sedge peats is 10-25 times higher, or more, in comparison with the content of it in the plant. In woody (alder) peats, there is from 2 to 30 times more sulfur than in the plant as a whole, never the same amount. With a Clarke of sulfur in the Earth's sedimentary mantle of 0.05% [16], lowland peats can be considered intensive sulfur concentrators. The peats of raised bogs, sphagnum ones, for example, do not differ from the plants in sulfur content. Consequently, the sulfur content of upland peats is constitutional, as it were. The distribution of sulfur through the stratigraphic section of peat deposits is comparable, in general terms, with the distribution of pyrite, i.e., the greatest pyrite content in the sediments of peat deposits corresponds, in most cases, to the greatest concentrations of sulfur. In accordance with this, the distribution curves of sulfur and pyrite in the cross sections of peat deposits (see Figs. 2, 5, 6, and 11, and Figs. 12 and 13) are similar to each other in configuration. This lets us draw the conclusion that the greater part of the total sulfur in sediments of peat deposits belongs mainly to sulfide sulfur and has a biogenic origin. This is indicated by the overall correlation of the sediments' sulfur content and the scale of development of sulfate-reducing bacteria in them. With an overall uneven distribution of sulfur in the layers of lowland peat deposits, for the overwhelming majority of them a tendency is noted, on the whole, toward a greater or lesser increase in its content in the direction of deeper layers of the peat bed, as, for example, in boreholes 4, 8, 80, 51, 87, 81, 83, 239, 43, 42a, 89, 120, 119, 46, 116, 105, and 44 (see Table 1), and boreholes 217, 501, 202, 238, etc. (see Figs. 2-4, 7, etc.). Such a pattern is primarily due to the prolonged action of the sulfate ions of seawaters on the peat bogs in the process of accumulation of organic matter in them (see below for greater detail).

A definite correlation is observed between higher or lower total sulfur content in lowland peat bogs, and the botanical composition of the genetic types of sediments and the degree of biochemical decomposition of their OM. The absolute amounts of total sulfur content are practically the same in the same genetic types of sediments, other conditions (ash content, depth of occurrence, and distance from the Black Sea coast) being equal, although they can vary significantly (see Table 1).

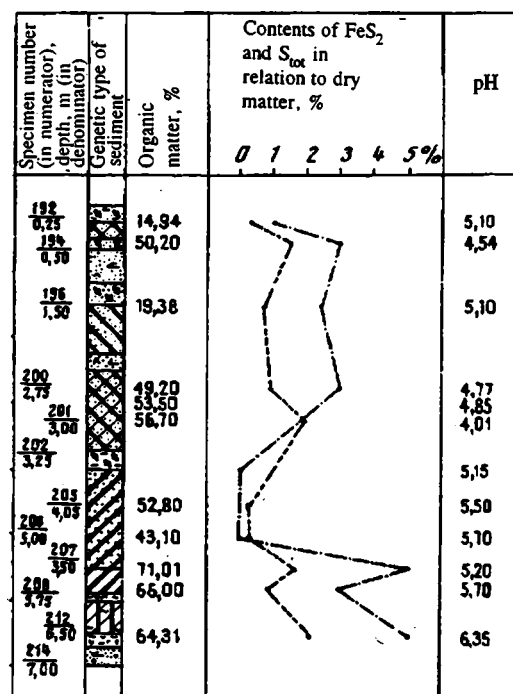


Fig. 12. Distribution of pyrite and total sulfur through borehole 11 (Anaklia peat deposit).

Thus, for borehole 105 (Imnat deposit), in specimens 69, 70, and 72, which are represented by sedge-reed, gelinite-precollinite, clayey peat, the total sulfur content varies from 2.3 to 2.4%, with depths of occurrence from 0.25 to 2.25 m. For borehole 8 (Anaklia deposit), in specimens 143 and 144, represented by woody, gelinite-precollinite, slightly clayey peat, the amount of total sulfur is 0.57 and 0.70%, respectively, and the depths of occurrence are limited to the peat-forming layer. For borehole 81 (Churia deposit), in specimens 863 and 628, from depths of 3.0 and 4.5 m, in the same genetic types (sedge-woody, gelinite-precollinite, clayey peat) the amount of total sulfur varies from 0.15 to 0.40%. In specimens 5 and 6 from borehole 217 (Grigoleti deposit), represented by woody, gelinite-precollinite, strongly clayey peat (depths 1.40 and 1.75 m), the total sulfur content is 0.14 and 0.30%, respectively. Analogous interrelations can also be observed for other boreholes (for example, boreholes 13 and 116 of the Imnat deposit, borehole 15 of the Kobuleti deposit, etc.).

If we take the same genetic types for different boreholes (for example, boreholes 51 and 87 of the Churia deposit): specimens 740 (depth 1.50 m) and 377 (depth 0.75 m), respectively, which are represented by rhizoid-sedge, gelinite-telinite, slightly clayey peat with gelinite-precollinite, then the total sulfur content varies from 0.22 to 0.50%. A certain difference in the amount of total sulfur consists in the fact that borehole 87 is further from the Black Sea coast (see below).

From this, we can draw the conclusion that genetic types of sediments of the same botanical composition and the same degree of biochemical decomposition, other conditions being equal, have the same or very close contents of total sulfur.

We will see if there is a dependence of total sulfur content on different degrees of biochemical decomposition, the various original plant material, i.e., the structure of the peat's OM, and, naturally, on the ratio of organic and mineral matter in sediment of a particular genetic type. Thus, for borehole 217 (Grigoleti deposit) specimen 279 from a depth of 0.5 m is represented by woody, gelinite-precollinite, clayey peat and contains 1.02% total sulfur, while specimen 281 from a depth of 1.5 m, which corresponds to woody, gelinite-telinite, clayey peat, contains 3.48%. Consequently, the structure of the OM has a decisive significance in the accumulation of total sulfur. A telinite structure, as less dense and "looser" in comparison with precollinite, promotes freer access of seawater into peat bogs, thanks to which the total sulfur content rises sharply (by more than three times).

Unfortunately, there are no more analogous examples, since the organic matter mostly has a precollinite structure, and the genetic types of sediments in which sandy, silty, or clayey material predominates are also combined with OM with a precollinite structure (with the exception of borehole 120, Pichora deposit, specimen 172, where the clay contained gelinite-posttelinite, woody peat).

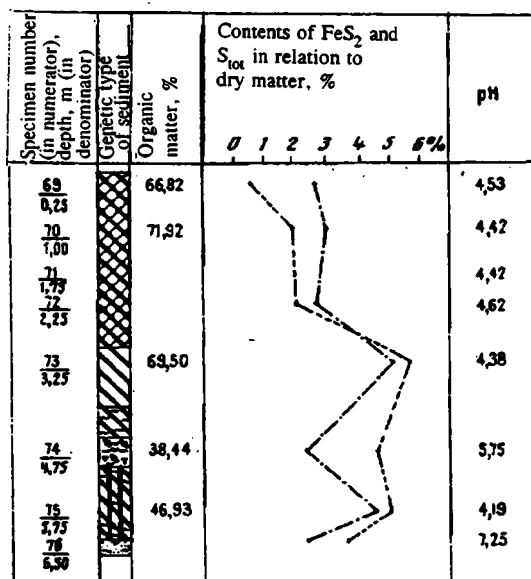


Fig. 13. Distribution of pyrite and total sulfur through borehole 105 (Imnat peat deposit).

If we turn to the genetic types of peat formed by herbaceous phytocenoses, then a complete dependence of sulfur content on the genetic type of sediment is observed here. Thus, for borehole 239 (Nabad deposit), specimen 1a (rhizoid-sedge, gelinite-telinite peat with gelinite-precollinite) contains 2.8% total sulfur, with a depth of occurrence of 0.5 m, while in borehole 87 (Churia deposit) specimen 377 (rhizoid-sedge, gelinite-telinite, slightly clayey peat with gelinite-precollinite), with an almost analogous depth, contains only 0.22% total sulfur. A similar pattern can be observed in some other boreholes (for example, borehole 51 of the Churia deposit, specimen 740; borehole 11 of the Anaklia deposit, specimens 205, 207, and 208). Unfortunately, the material is limited here also. And finally, the genetic types of moss bogs are characterized by very low total sulfur content (boreholes 14 and 15 of the Kobuleti deposit).

SOURCE OF TOTAL SULFUR IN PEAT BOGS

Since the amount of "constitutional" sulfur, as was shown above, is fairly low and constant for all genetic types of sediment, sharp variations in sulfur content in a particular type of sediment are primarily caused by the entry of sulfur in the form of sulfate from external sources. To confirm this conclusion, we studied the areal distribution of sulfur in peat deposits of Colchis. As a result, we found a clearly expressed pattern, which consists in a decrease in sulfur in genetic types of sediments of the cross sections of peat deposits in the direction away from the Black Sea coast and into the interior of the region of peat accumulation, and also with distance from the mouths of rivers and from lakes that have a connection with the sea. Thus, for example (see Table 1 and Fig. 1), in the genetic types of sediments of borehole 11 (Anaklia deposit), which is located near the Black Sea coast, significantly more sulfur is noted, on the whole, than in the sediments of borehole 8 (the same deposit) further from the coast. There is another clear example along the profile of boreholes 52-51-87-81 (Churia deposit, see Table 1 and Fig. 1) situated in order of increasing distance from the seacoast into the interior of the Colchian lowland, for which we can see a steady reduction in the sulfur content of various genetic types of sediments with distance from the sea. A similar clear pattern is also observed for boreholes 239 and 43 (Nabad deposit). All of the genetic types of sediments of borehole 239 contain many times more sulfur than the sediments of borehole 43, which is located further from the sea.

The fact of increased sulfur content in sections of peat deposits adjacent to the mouths of river (see Fig. 1) is illustrated by the cross sections of borehole 10, which is located near the mouth of the Churia River (Churia deposit), borehole 243 in the marginal part of a peat bog on the bank of the Tikora River, and borehole 217 (Grigoleti deposit), which is located in the part of the peat bog in contact with the waters of the Dedaber River (now a canal) and has a connection with the sea through the Moltakva and Koparchi Rivers. There is a rather large amount of sulfur in various genetic types of

TABLE 3. Contents of Sulfate Ions, Chlorine Ions, and Iron in Waters of Rivers of the Colchian Lowland, mg/liter

Place where sample was taken	Distance from sea-coast, km	Time when sample was taken	Mineralization, mg/liter	SO ₄ ²⁻	Cl ⁻	Fe _{tot}
Mouth of the Inguri R.	0,02	X/1971	195,0	23,00	14,0	None
	0,1	X/1971	180,0	18,0	6,0	"
	0,2	X/1975	152,0	17,28	10,64	0,02
Inguri R.	3,2	X/1975	154,0	16,32	9,93	0,04
	9,0	X/1975	148,0	14,40	11,35	0,05
Mouth of the Tikora R.	0,03	X/1971	1238,0	87,41	553,18	None
Mouth of the Churia R.	0,03	X/1975	208,0	19,20	65,25	0,13
Mouth of the Khobi R.	0,03	X/1975	164,0	11,52	17,02	0,10
Khobi R.	3,8	X/1975	170,0	9,60	12,06	0,05
From mouth of the Tsivi R. (upstream)	2,3	X/1975	98,0	13,44	10,64	0,14
Lake Narto-Tskali	1,2	X/1975	90,0	17,28	10,64	0,10
Rioni R.	5,6	X/1971	264,0	18,24	49,64	0,01
	30,0	X/1971	146,0	6,72	None	0,02
	0,4	X/1975	220,0	23,04	69,35	0,02
	5,8	X/1975	188,0	21,12	8,87	0,02
	22,3	X/1975	180,0	None		0,04
Mouth of the Pichora R.	0,02	X/1971	178,0	140,0	921,0	—
	5,5	X/1971	177,0	38,0	14,0	—
	7,5	X/1971	196,0	35,0	10,0	—
	19,0	X/1971	229,0	4,0	8,0	—
Mouth of the Kukani R. (where it flows into the Pichora R.)	12,0	X/1971	182,0	21,10	30,90	None
Central part of Lake Paliastomi	4,0	X/1975	953,0	648,00	4758,73	0,01
Kaparcha R.	4,4	X/1975	170,0	21,12	107,80	0,05
Mouth of the Supsa R.	0,02	X/1975	150,0	26,88	39,01	0,02
	5,0	X/1975	112,0	11,52	11,34	0,04
	7,9	X/1975	112,0	14,40	9,34	0,02
	12,9	X/1975	108,0	24,96	8,86	0,02
Mouth of the Natanebi R.	0,01	X/1975	72	2,59	6,38	None
Mouth of the Choloki R.	0,01	X/1975	65	None	6,38	—
Kintrishi R.	0,15	X/1975	80,0	3,84	0,08	0,12
	2,5	X/1975	82,0	3,84	0,08	0,02
	5,7	X/1975	64,0	3,84	0,08	0,01
Black Sea (in the region of Grigoleti)		X/1971	13396	998,00	7027,82	0,04
Precipitation:						
In the region of Moltakva		X/1971	10,85	2,00	1,34	—
In the region of Kobuleti		X/1964	47,0—68,88	5,71—10,70	4,45—25,0	
			Sometimes as much as 197.61	Sometimes as much as 25.50	Sometimes as much as 88.88	

sediments in the cross section of borehole 105 (Imnat deposit), which is adjacent to the east shore of Lake Paliastomi, and borehole 127 (Moltakva deposit), which adjoins it on the south. The sediments of borehole 116, which is far from Lake Paliastomi and in the same profile with borehole 105 (Imnat deposit), contain comparatively little sulfur. The genetic types of sediments in cross sections of boreholes in the central parts of lowland bogs, and also the margins on the side of the dry land, display significantly less sulfur. Besides the ones mentioned above, such boreholes include 42a and 231 (Nabad deposit), 83 (Churia deposit), 129 and 215 (Grigoleti deposit), etc., which are located within the bounds of lowland bogs, and also the cross sections of peat beds in raised bogs, represented by boreholes 46, 13, and 24 (Imnat deposit), and 14 and 15 (Kobuleti deposit). Low sulfur content is characteristic of the genetic types of sediments of boreholes 123 and 121, in spite of the fact that they are located directly on the north shore of Lake Paliastomi. This phenomenon is explained by peculiarities of the hydrological and hydrochemical conditions in this part of the region of peat accumulation, of which more will be said in the next communication, which is devoted to the distribution of iron sulfides in peat deposits of Colchis.

We will consider the contents of sulfate ions in the waters of rivers, lakes, and bogs in the region of peat accumulation. The data in Table 3 indicate an overall rise in contents of sulfate ions in rivers and lakes draining the region of peat accumulation of the Colchian lowland. Thus, the Inguri, Churia, Khobi, Tsivi, Rioni and Supsa Rivers, and Lake Nartotskali, with mineralization of their waters from 100 to 200 mg/liter or more, contain from 11 to 26 mg/liter of sulfate ions. In regions of peat accumulation of the intracontinental type (for example, in Belarus), rivers and lakes connected with regions of peat accumulation contain sulfate ions in the range of 3-5 mg/liter, and concentrations of it in the amount of 15 mg/liter are found extremely rarely [15]. Against the general background of increased sulfate content in waters of the enumerated rivers of the Colchian lowland, anomalously high contents of sulfate ions are characteristic of the mouths of the Tikora (87 mg/liter) and Pichora Rivers (140 mg/liter), the Moltakva River over its whole extent from the sea to Lake Paliastomi (96-189 mg/liter), and the waters of Lake Paliastomi (648 mg/liter). In the Black Sea, the sulfate content is 998 mg/liter. Anomalously low contents of sulfate ions are characteristic of the Natanebi, Choloki, and Kintrishi Rivers. In them (with mineralization of their waters from 64 to 82 mg/liter), the contents of sulfate ions do not exceed 2-4 mg/liter and do not increase, even at their mouths. As we can see from Table 3, in almost all of the rivers of the Colchian lowland, with the exception of the Natanebi, Choloki, and Kintrishi, the contents of sulfate ions are noticeably higher near their mouths in comparison with sections of the rivers far from their mouths. Thus, for example, the mouth of the Inguri River contains from 17.28 to 23 mg/liter of sulfate ions, while upstream the waters contain 16.32-14.40 mg/liter. At the mouth of the Supsa River, sulfate ions are present in the amount of 26.88 mg/liter; and 5 km upstream, 11.52 mg/liter. The Pichora River is an especially clear example: at its mouth, sulfate ions amount to 140 mg/liter, while upstream the concentration of them drops sharply, but stays high for more than 7 km, only decreasing to 4 mg/liter 19 km from the mouth.

It is typical that, in all cases, a reduction in the concentration of sulfate ions in the water is clearly controlled by an even greater reduction in the concentration of chlorine ions, which are, as is known, an indicator of the sea's participation in formation of waters' salt composition.

From Table 3, we can also see that, in all rivers of the Colchian lowland, except for the Natanebi, Choloki, and Kintrishi, increased contents of chlorine ions are noted, especially near their mouths, and the concentration of chlorine ions in the water correlates with the concentration of sulfate ions. This indicates significant penetration of seawater into the enumerated rivers of the Colchian lowland, and the marine origin of sulfate ions in their water. In contrast to this, the sea only has a slight effect on formation of the salt composition of the waters of the Natanebi, Choloki, and Kintrishi Rivers, as a consequence of their steeper profile and greater flow rate in their lower reaches in comparison with the Inguri, Khobi, Rioni, and Supsa Rivers, etc., the waters of which contain many times more sulfate and chlorine ions. As far as the groundwaters feeding lowland peat bogs of Colchis, according to the data of V. A. Sikharulidze, L. A. Kharatishvili, V. I. Beselii et al. (background material), an especially sharp increase in their overall mineralization is noted in a coastal strip 1.5-2 km wide. This takes place, the authors believe, on account of sharp concentration of chloride-sodium salts in connection with the effect of seawater, in which sulfate ions are the third component. The mineralization of groundwaters in the coastal strip, as the research of I. P. Mikadze, L. A. Kharatishvili, and N. V. Dolidze show (background material), depends on the tides and precipitation. The sea's greatest effect on formation of the salt composition of groundwaters in the coastal strip, according to their data, is in the dry time of year. In connection with this, the water's overall mineralization rises, and many ions of marine origin appear in its composition. The increased concentration of sulfate ions near the mouths of rivers, in lakes that have a connection with the sea, and in groundwaters of the coastal strip of the Black Sea ties in well with the revealed patterns of distribution of sulfur in the area of peat accumulation of the Colchian lowland. Consequently, sulfur entered peat

TABLE 4. Contents of Sulfate Ions, Chlorine Ions, and Iron in Peat-Bog Waters of the Colchian Lowland, mg/liter

Place where sample was taken	Genetic type of sediment	Mineraliza- tion, mg/liter	SO ₄ ²⁻	Cl ⁻	Fe _{tot}
Western edge of bog, 0.15 km from seacoast. Black Sea coast south of Okumi R. (703)	Gray-brown clay, with lump structure, rootlets of woody plants, and attritus (contemporary soil)	143.0	206.40	468.07	0.55
Western edge of Zorgat bog, 0.5 km from seacoast (711)	Sedge-reed, gelinite-precollinite, clayey peat	80.0	None	21.99	0.20
Western edge of Anakli bog, 0.5 km from seacoast (700)	Sand of medium and varying grain size brownish-gray, with herbaceous attritus in lower part	224.0	53.76	66.66	0.25
On bank of Tikora R., 0.5 km from its inflow into the sea (243)	Gray-brown clay, with lumpy structure, rootlets of woody plants, and diatoms	142.0	5.76	29.79	0.65
Eastern edge of Churia bog, 6 km from seacoast (370)	Woody, gelinite-precollinite, clayey peat	168.0	1.44	4.61	0.04
Western edge of Nabad bog, 0.8 km from seacoast (239)	Rhizoid-sedge, gelinite-telinite peat with gelinite-precollinite	125.0	Trace	18.44	0.07
Eastern edge of Nabad bog, 6.5 km from seacoast (230)	Sedge, gelinite-precollinite peat	61.0	6.72	5.67	0.01
Eastern edge of Nabad bog, 9 km from seacoast (238)	Gray-brown clay with lumpy structure and rootlets of woody plants (contemporary soil)	118.0	None	4.26	0.01
Central part of western edge of Moltakva bog, 1 km from seacoast (208)	Woody, gelinite-precollinite, clayey peat	118.0	"	26.0	0.01
Western part of wouthern edge of Moltakva bog, 1 km from seacoast (204)	Gray-brown clay with lumpy structure and rootlets of woody plants (contemporary soil)	100.0	9.83	14.89	0.04
Western part of southern edge of Moltaka bog, 0.4 km from seacoast and 0.6 km from channel of the Supsa R. (203)	Fine-grained, clayey, grownish-gray silt with rootlets of woody plants (contemporary soil)	99.0	21.21	37.33	0.01

Remark. The samples were taken in October 1971.

bogs of the lowland type in the form of sulfate ions, and its concentration was determined by the concentration of sulfate ions in the groundwaters and river waters feeding them. This is also confirmed by the fact of very low sulfur content in peat bogs of the raised type, as was shown previously (see Table 3) on the examples of boreholes 124 and 46 (Nabad peat bog), and boreholes 14 and 15 (Kobuleti peat bog). The latter are fed by water from precipitation, which, as a rule, has very low concentration of sulfate and chlorine ions. Thus, in the region of the Moltakva River precipitation contains 2 mg/liter of sulfate ions and 1.34 mg/liter of chlorine ions, with overall mineralization of 10.85 mg/liter. In the region of Kobuleti, according to data from the hydrometeorological station [11], the concentration of sulfate ions in precipitation in the zone 1-1.5 km from the seacoast varies from 5.71 to 11 mg/liter during the year, rising to 25 mg/liter in rare cases (see Table 3). However, the peat bogs in Kobuleti are located outside of this zone.

Table 4 give data on the contents of sulfate and chlorine ions in peat-bog waters of the Colchian lowland, from which it follows that the waters' mineralization varies in a wide range (from 61 to 224 mg/liter), but on the whole it is somewhat lower than the mineralization of river waters feeding peat bogs in northern and central parts of the Colchian lowland (see Table 3). The contents of sulfate ions also vary in a wide range (from 206 mg/liter to analytic zero). Low contents of sulfate ions (6.72-1.44 mg/liter) or their absence are characteristic of peat-bog waters on the eastern margins of the regions of peat accumulation, which are fed by waters formed without any significant influence of the sea. This is indicated by the very low (4.26-5.67 mg/liter) contents of chlorine ions in the peat-bog waters, for example, samples from boreholes 370, 230, and 238. The low content of sulfate ions (9.83-5.76 mg/liter) characteristic of peat-bog waters on the western margins of regions of peat accumulation (water samples from boreholes 711, 243, 239, 208, and 204) is explained by desulfatization of the feed waters due to reduction of sulfate ions in them. The initially higher concentration of sulfate ions in the water feeding these sections of the peat deposits is indicated by the significant contents of chlorine ions in the peat-bog waters, and also by the fairly high sulfur content of the sediments, for example, borehole 243 of the Tikora deposit and 239 of the Nabad deposit (see Table 1). K. I. Lukashev, V. A. Kovalev et al. [15] consider the fact of desulfatization of bog waters in regions of peat accumulation in Belarus as a reflection of processes of early diagenesis of bog deposits.

In the final analysis, what determines the characteristics and quantitative distribution of sulfate-reducing bacteria in cross sections of peat bogs represented by specific and, at the same time, diverse genetic types of sediments? The latter include genetic types of peats with one or another amount of terrigenous-clay material, as well as sandy, silty, and primarily clay sediments with different degrees of peatiness or a small content of organic matter.

From the analysis given above of the distribution of sulfate ions of seawater in peat bogs, expressed in a particular amount of total sulfur,** it follows that, other conditions being equal, it is directly related to the genetic types of sediments, the basic components of which are the ratio of organic and mineral matter, the nature and type of peat-forming plants and the structure arising as a result of biochemical decomposition of their tissues: woody, herbaceous, and moss peat-forming plants. The amount of sulfate ions of seawater entering into a peat bog and forming the hydrogeochemical characteristics of groundwaters depends on the location of the peat bogs' cross section in relation to the coastline of the Black Sea. On the whole, the closer the edge of a peat bog is to the strand line, the more sulfate ions of seawater penetrate into it and, consequently, the greater the amount of total sulfur it contains.

But there are differences here. The mouths of rivers, into which seawater penetrates in large amounts practically without obstruction for a certain distance (in conditions of a vast lowland with small slope of the rivers' channels) are more favorable areas. They are in direct contact with peat bogs, and in accordance with their genetic nature an increased amount of total sulfur accumulates in their marginal parts in comparison with the rest of the coastal area. The combination of these facts (the genetic type of sediments and their location in relation to the coastline) determines the localization of zones of intensive bacterial sulfate reduction, the sources of total sulfur, and the spatial and temporal distribution of it in the cross sections of peat deposits. The further from the strand line of the Black Sea a particular type of genetic sediments is, the less total sulfur in it, and vice-versa. Moss raised peat bogs practically do not come into contact with sulfate ions of seawater, and therefore they are characterized by quite insignificant amounts of total sulfur.

The quantitative distribution of total sulfur through the cross section also depends on the depth of occurrence of sediments of particular genetic types. It was mentioned above that, other conditions being equal (the same genetic types and distances from the strand line), the lower horizons of peat bogs contain a larger amount of total sulfur as a result of intensive

** This also includes the sulfur of peat-forming plants, which practically does not affect the balance of total sulfur.

and prolonged penetration of seawater into them. This is also promoted by the structure of organic matter, that is to say, telinite is more favorable than collinite. There are exceptions in two cases: 1) if the peat bog has a complex structure, i.e., it contains interlayers of terrigenous or clay sediments, especially the latter, then the lower-lying genetic types may have a lower content of total sulfur, or the amount of it does not increase as quickly down through the cross section; 2) if the peat bog may have been located at a different distance from the waterline at certain times in the process of its formation.

Thus, comprehensive lithological and facial analysis of the formation of peat deposits in the Colchian lowland of the Rioni intermontane trough made it possible to clarify features of the hydrochemical nature of total sulfur, which is the result of enrichment of peat bogs with sulfate ions from the Black Sea. This enabled us to determine the localization of zones of intensive bacterial sulfate reduction, the sources of sulfur, and its spatial distribution in peat bogs of Colchis.

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PRESENT-DAY SUBMARINE HYDROTHERMAL ACTIVITY IN THE TAUPO-ROTORUA ZONE (BAY OF PLENTY, NEW ZEALAND)

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We made detailed descriptions of the structure and material composition of sedimentary and water columns in the vicinity of active submarine hydrothermal activity in the southern part of the Bay of Plenty (North Island, New Zealand). Geophysical methods revealed that the hydrothermal system is confined to a tectonically distinct zone with a sedimentary cover characterized by complex structure. Chemical and mineralogical investigations confirmed that the activity of underwater vents exerts no substantial regional influence on the composition and features of ore mineralization in these formations. It is shown that essentially hydrothermal formations distinguishable within areas of otherwise monotypic sediments directly coincide with zones of hydrothermal discharge in the ocean floor. The absence of pronounced hydrothermal anomalies, together with the presence of "tongues" of anomalous concentrations of water-soluble gases suggests that the discharges are primarily hydrothermal in character.

The study area is located in the southern part of the Bay of Plenty (North Island, New Zealand) between the White and Whale volcanic islands (Fig. 1). The geological structure of the region is a result of its position in the seaward continuation of the active Taupo-Rotorua volcanic zone (TRVZ). In the bottom topography of the southern part of the Bay of Plenty, the continuation of the TRVZ is clearly evident in the form of a north-eastward striking zone (40 × 150 km) [9], characterized by hilly topography with ridges and valleys. This zone is centrally located within the shelf of the bay (encompassing a portion of the continental slope) and is separated from flatter zones to the east and west by two large-scale lineaments. These tectonic elements are interpreted as continuations of large-scale faults on land forming the boundaries of the TRVZ depression [8]. In the bottom topography, they are represented by scarps on a slope; at their northern end, these scarps are associated with parallel-running canyons and troughs. Two andesite-dacite volcanoes are located directly within the central zone: the collapsed Matuhora volcanic edifice (Whale island), situated within the shelf, and the currently active volcano of White Island rising above the ridge by the same name at the transition between the shelf and continental slope. Both island-volcanoes are in line with a row of volcanoes on the landward side of the TRVZ.

Within the study area, present-day submarine hydrothermal activity can be reliably identified in the water column on the basis of hydroacoustic anomalies [10, 13] and can be directly observed operators of manned submersibles [19] and divers. Investigation of the present-day hydrothermal activity in this region is certainly relevant to assessment of the influence of such activity on the chemical composition and mineralization of bottom sediments and its effect on the surrounding seawater. The scientific literature now includes a substantial number of publications concerning present-day submarine hydrothermal activity in the Bay of Plenty [5-7, 10, 12-14, 18, 19, etc.]. However, any new information concerning occurrences of submarine hydrothermal activity in this region is of interest and deserves close examination. In this report, we present the results of combined geophysical, lithological-mineralogical, and hydrochemical investigations obtained during the 18th cruise of the R/V *Akademik Nesmeyanov* (1990) and during the 30th cruise of the R/V *Vulkanolog* (1988).

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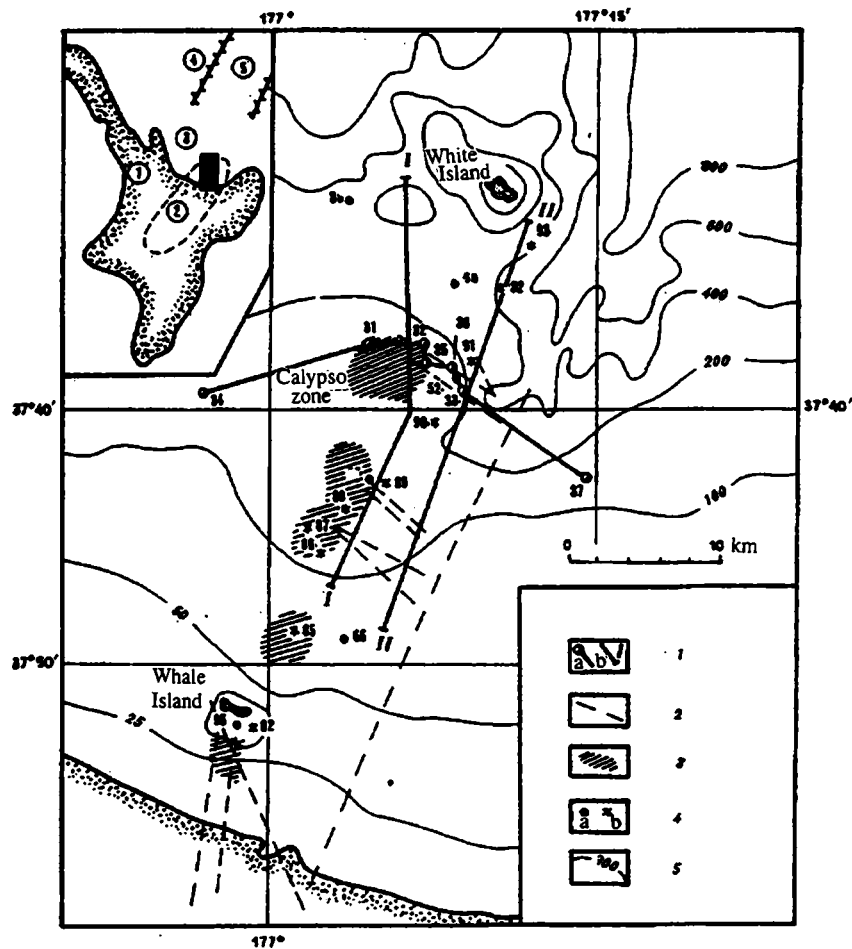


Fig. 1. Sketch map of area of operations in the southern part of the Bay of Plenty. 1) Line of discrete geochemical sampling in the area of the Calypso vent of present-day submarine hydrothermal activity (a) and continuous seismic profiles (b) (numbering of profile indicated by roman numerals); 2) faults discovered during the operations and known from published data [8]; 3) zones of discharge of gases at the ocean floor, identified by hydroacoustic anomalies in the water column; 4) stations for sampling bottom sediments by means of corers and numbering of stations: (a – 30th cruise of the R/V *Vulkanolog*, February-March, 1988; b – cruise of the R/V *Taranui*, June, 1970 [14]); 5) isobaths, m. The locations of the area of operations is shown in an inset. The following are designated by numbers: 1) North Island, New Zealand; 2) Taupo-Rotorua volcanic zone; 3) area of operations in the southern part of the Bay of Plenty; 4) Colville ridge; 5) Havre trough.

GEOPHYSICAL INVESTIGATIONS

Geophysical investigation of the study area was carried out along a series of subparallel traverses oriented NE–SW. The network of traverses was concentrated near Whale Island, where zones of active hydrothermal discharge were previously discovered to coincide with small isometric depressions [10]. Interpretation of single-channel continuous seismoacoustic profiling (CSP) data indicates that individual volcanic edifices and White Island ridge yield strong parabolic, seismically opaque reflections typical of rock belonging to volcanic basement (Fig. 2, profile II–II). The northeast strike of the volcanic structures (common for the Taupo-Rotorua volcanic zone) is controlled by faults. Negative topographic forms are filled with sediments not exceeding 150–200 m thickness at any location. The reflections suggest that the sediments are subhorizontally stratified. We assume erosion of anticlinal topographic forms during a phase when sea level remained at a constant elevation. The surficial layers of the sedimentary cover are occasionally disturbed by consedimentary slumps.

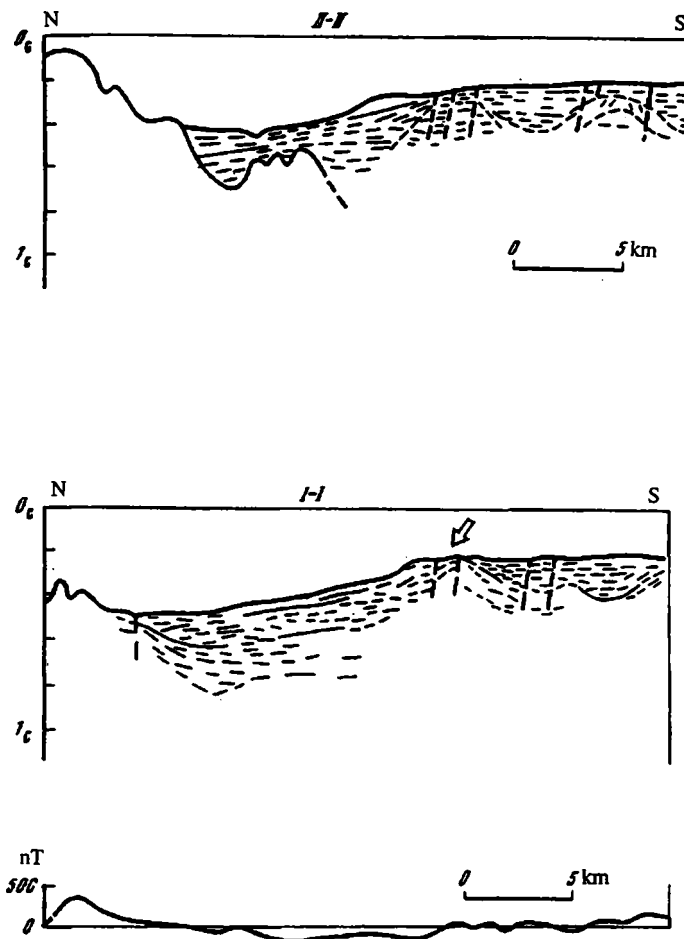


Fig. 2. Interpretation of seismogram fragments along CSP profiles I-I and II-II (for positions of profiles, see Fig. 1). Positions of reflectors and faults are shown in the sections. The vertical scale on the sections is given in seconds of double time for signal propagation. A graph showing an anomalous magnetic field is provided for profile I-I. The position of the Calypso vent of present-day submarine hydrothermal activity is indicated with an arrow.

Another interesting feature of the sedimentary section of the region is the presence of layers which continue upward into the topmost bedding and pass downward into layers covering the bottom (see Fig. 2, profile I-I). This indicates a transition from a depositional environment with active hydrodynamics to conditions of poor water circulation, an environment probably also caused by periodic fluctuations in sea level.

Scarps (which can be correlated on adjacent profiles) with amplitudes not exceeding 20-30 m can be identified on seismograms of shelf areas. Most of these are associated with normal faults, with the greatest number of such faults restricted to the outer shelf. It should be noted that faults, the main tectonic structures, and gently folded forms in the sedimentary cover trend northwest.

Reflections from beneath the ocean floor at the shelf edge reveal a pronounced domal structure. It is interesting that its peak coincides in plan with the position of an on-going zone of submarine hydrothermal activity referred to in the scientific literature as "Calypso" [19] (see Fig. 2, profile I-I).

Volcanic structures of White Island ridge show up in the anomalous magnetic field of the study area. They are characterized by positive anomalies ranging from 250 to 600 nT and constitute the northern end of a belt of magnetic anomalies of the Taupo-Rotorua volcanic zone associated with a chain of andesitic volcanoes and continuing for a distance of 250 km [5]. Most of the magnetic anomalies of the two-maximum variety coincide with conical topographic forms. Such anomalies suggest simple-shaped magnetic bodies magnetized in accordance with the present-day geomagnetic field. Within

the inner shelf, local positive anomalies of small amplitude probably coincide with cores of anticlinal folds. The absence of pronounced magnetic anomalies at sites of on-going discharge from submarine vents deserves attention.

LITHOLOGICAL INVESTIGATIONS

The peculiarities of the composition of the bottom sediments in the seaward continuation of the Taupo-Rotorua volcanic zone are a result of the location of the study area at the boundary of two regions with substantially different environments of sedimentogenesis: the nonvolcanic (eastern) and the volcanic (western) zones of the Bay of Plenty. These regions are clearly differentiable on the basis of bathymetric, geophysical, and lithological characteristics. Sediments of the eastern zone, which sharply predominate in the study area, are represented by greenish-grey Holocene muds predominantly formed as a result of erosion of greywackes of Mesozoic age from the axial ridges of North Island. The Holocene sedimentary prism, with a thickness on the order of 20 m according to J. P. Glasby [17], thins toward the shore and in the direction from the continental slope to the boundary of the inner shelf, where it is replaced by intermediate- and fine-grained sands with sparse greywacke pebbles. The sand fraction, accounting for 10-25% of the total in Holocene sediments of the region, is represented by feldspathic sand with large quantities of vesicular rhyolite glass. A similar composition is characteristic of the sediments of the western zone of the Bay of Plenty; their origin has been linked to the on-going volcanic activity within the Taupo-Rotorua volcanic zone. The main lithological variations of bottom sediments within the area of occurrence of the Holocene mud prism are linked to occurrences of well developed white layers of rhyolitic ash (which can be correlated with dated eruptions of volcanoes within the Taupo-Rotorua volcanic zone [17]), interlayers of shelly detritus, and volcanoclastics. The latter are a product of andesitic explosions of White Island and occur within a radius of 15-20 km from the island (gradually decreasing in quantity with distance from the island).

The ratio of the clay fraction to the sand fraction in monotypic sediments shows negligible variation along section and over the area. The clay fraction shows a clear quantitative predominance, constituting 75-90% of the total rock. This type of sediment is mineralogically similar to formations of the glauconite type [4]. Dioctahedral layer silicates predominate in the composition of the clay fraction; such silicates include: hydromica, smectites (montmorillonite, nontronite, and beidellite), and kaolinite. X-ray-phase and electron-microscope investigations also revealed iron-magnesium chlorite, halloysite, mordenite, calcite, and hydrous ferric oxides. Two mineral zones can be distinguished on the basis of relative mineral content in the clay fraction, the distribution of such minerals along the section in the most clayey fraction (Table 1), and their distribution along the section in the most representative sedimentary cores (B-30-95 and B-30-63). These zones are 1) predominantly hydromica (up to 70%) and chlorite (up to 30%) (chlorite-hydromica zone); 2) predominantly hydromica (up to 53%) and smectite (up to 41%) (hydromica-smectite zone). There is a substantial quantity of smectite in the interval of 100-120 cm. Both zones contain fossils of diverse life forms with carbonate and opaline skeletons.

The ore mineralization in the bottom sediments in this study area deserves special attention. Low-temperature (15-22°C) gas-hydrothermal seeps have been discovered at depths of 12-15 m in the western nearshore area of Whale Island. These seeps coincide with hydrothermal formations of several types: powdery coatings or incrustations on the surfaces of boulders; sandy aggregates cemented by sulfide material and also pseudomorphs developed from organic forms and accompanied by the formation of finely crystallized aggregates. The main characteristic of the low-temperature sulfides found in this area of present-day hydrothermal activity is their close paragenetic association with magnetite. Almost all of the ore formations consist of magnetite crystals replaced on the outside, to one degree or another, by sulfides. A "monomineralic" sulfide phase sampled under the microscope during treatment with hydrogen peroxide proved to consist of 2/3 magnetite. The sulfide component showed the following composition: Fe 37.5%; Mn 591 mg/g, Zn 502 mg/g; Cu 57 mg/g; Ni 141 mg/g; this suggests that the predominant sulfide is pyrite. Pseudomorphs of pyrite after magnetite indicate a metasomatic origin for sulfides formed as a result of seepage of hydrogen sulfide through magnetite-bearing sand. The concentrations of microelements matches a diagenetic analog from the Black Sea sediments [1]; this is a substantially better match than in pyrites of high-temperature hydrothermal springs [2]. In the most thoroughly studied core of sediments (B-30-95) collected from this zone, there is a regular increase in the quantity of sulfides downward along the section of the column. In the interval 5-10 cm from the surface of the sediments, the portion of ore minerals equals approximately 3% of the rock volume; in the interval 48-50 cm from the surface, it equals 8-10%. It should be noted that the character of ore mineralization in this column closely corresponds to variations in the physical-chemical parameters of the sediment here, in particular, to the increase in the temperature of the sediments to 82.5°C and the decreases in the pH and Eh in the lower part of the column as well as the

TABLE 1. Relative Abundances of Minerals in the Pelitic Fraction (less than 0.01 mm) of Bottom Sediments in the Southern Part of the Bay of Plenty, %

Sample No.	Sampling interval, cm	Hydromica	Chlorite	Smectite	Quartz	Calcite
95/1	0—5	64	29	7	—	—
95/2	38—40	65	24	11	+	—
95/3	78—80	68	27	5	+	—
95/4	118—120	60	34	6	—	—
95/5	157—160	41	8	54	—	—
52/1	0—2	65	23	12	—	—
52/2	50—52	57	30	13	—	—
55/1	0—2	51	37	12	—	—
55/2	106—108	49	33	18	+	+
63/1	0—2	64	29	6	—	—
63/2	109—110	57	29	14	—	—
66/1	0—2	69	26	5	—	—
66/2	65—66	61	22	17	—	—

Explanation. 1. The number of the sampling site is given in the numerator of the sample number and the number of the sampling horizon is given in the denominator. 2. "-" sign indicates absence of the mineral; "+" sign indicates presence of the mineral. 3. Results of the interpretation of data from x-ray phase analysis (carried out at the Central Laboratory of the Industrial and Scientific-Research Institute for Engineering Investigations of Construction are given in the table.

increase in the quantity of sulfur with depth [7]. In columns collected from sediments outside the zone of present-day hydrothermal activity, the content of the ore component is substantially less.

GEOCHEMISTRY OF BOTTOM SEDIMENTS

Analysis of the distribution of rock-forming elements and several dispersed elements in samples of bottom sediments collected along a traverse between Whale and White islands suggests slight variation in the chemical content of rock both along the this profile and along the section of the upper part of the sequence we investigated. The contents of the majority of elements in these samples (Table 2) closely match their concentrations as reported in [14] based upon sediment columns collected near these sites. In turn, both these samples of the chemical composition of the rock reflect features characteristic of volcanogenic rocks of intermediate composition; this is in agreement with suggestions [12] that the erosion products of Mesozoic andesitic greywackes of North Island axial ridges dominate the composition of the sediments in the study area and that Quaternary acidic volcanites of the TRVZ play a subordinate role. This is very evident on a diagram (Fig. 3) composition fields for respective samples are compared with the position of a reference line showing compositions of andesitic greywackes normalized to the composition of sediments which show no enrichment with metals [12]. On this diagram, it is clearly apparent that the hydrothermal clays directly sampled from one of the gryphons in the present-day Calypso hydrothermal zone by a manned submersible [20] have a different composition characterized by extreme impoverishment with respect to Cu, Cr, and Mn. A very different distribution of elements occurs in the finely dispersed colloidal material precipitating at the sea water-acidic stream geochemical barrier near White Island [12]. In this case, abundances of all the components investigated are substantially greater.

In general, the chemical characteristics of the rock examined supports earlier conclusions [12, 14, 19] that there is no substantial enrichment of bottom sediments with metals due to recent hydrothermal activity in the zone investigated in the southern part of Bay of Plenty. With regard to this zone, one can only speak of local sites where the compositions of a number of elements are elevated. Near White Island, for example, the increases in concentrations of Fe, Mn, Zn, Ni, and Cr downward along the section [12] are a result of a change in the mineral composition of the bottom sediments; this, in turn, is a result of accumulation of mineral of the heavy fraction in the lower part of the bed reworked by waves. In the deeper

TABLE 2. Chemical Composition of Bottom Sediments in the Southern Part of the Bay of Plenty

Element	Number of samples	Average content	Standard deviation	Sample interval, cm
Fe	68	3,46	0,87	2,47—4,52
Ti	49	0,37	0,08	0,20—0,52
Mn	57	0,13	0,07	0,04—0,32
Co	38	19	6	10—32
Ni	57	50	32	10—115
Cu	57	48	31	15—147
Zn	68	79	22	28—146
Rb	49	86	12	47—102
Sr	49	239	23	185—284
Y	49	21	4	13—27
Zr	49	174	14	130—199
Nb	49	8,5	3,1	0,3—13,1
Mo	49	4,6	1,6	1,7—8,5
Hg	62	11,5	10,2	1,0—45,6

Explanation: 1. Contents of Fe, Ti, and Mn are given in wt%; Hg in $n \cdot 10^{-6}\%$, other elements in ppm. 2. Analyses carried out by means of atomic-absorption and x-ray radiometric methods at the Central Chemical Laboratory of the Dal'morgeologiya Northern Pacific Geological Expedition (Petropavlovsk-Kamchatskii), analytical chemists L. G. Osipenko and O. A. Cherenkova.

parts of the bay, where hydrodynamic activity is less, mineralogical and geochemical differentiation is not evident within the upper sedimentary bed (15-30 cm).

Essentially hydrothermal alteration of bottom sediments as a result of recent hydrothermal activity can be found only within monotypic sediments. One formation of this type is dark-grey silt collected at a depth of 40 m within the gas-hydrothermal field south of Whale Island [6, 7]. The temperatures of sediments at time of collection ranged from 17 to 82.5°C, which is characteristic of hydrogen sulfide reserves. Silt sediments collected outside the zone of present-day hydrothermal activity yielded temperatures 10-12°C, were greenish-grey, and do not outgas hydrogen sulfide. Examination of samples collected in the area of hydrothermal discharge indicates that the concentrations of easily mobilized phases of Fe, Mn, and Zn decrease with increasing temperature of the sediment, an increase which, in turn, reflects the intensity of hydrothermal reworking of silty terrigenous sediments. The abundances of reduced forms of these same metals increase simultaneously. Here, the sum of mobile species of Fe and Mn decreases with increasing temperature while Zn remains constant. Consequently, leaching of easily mobilized species of Fe, Mn, and Zn from sediments with partial (Fe, Mn) or complete (Zn) fixation of mobile metals within the composition of hydroxide phases takes place during hydrothermal reworking. The degree of hydrothermal reworking has a negligible effect on the total quantity of metals and content of mobile species of Cu and Ni in the clayey sediments around Whale Island.

Light-chocolate-colored aleuropelitic sediments directly coinciding with zones of hydrothermal discharge in sands near White Island are another variety of hydrothermally altered sediments in the southern part of the Bay of Plenty. Elevated contents of Fe, Ni, and Cu, due to high concentrations of lithogenic species of these metals (not recovered by the extraction system used), are typical of these sediments. These are probably products of hydrothermal reworking of volcanic rocks of White Island rich in crystallized hydrous iron oxides. In our view, the elevated contents of Fe, Ni, and Cu, found earlier in sediments near White Island [12] are a result of contamination with precisely this material.

Mercury content was determined for all samples of bottom sediments collected in the study area. Analysis revealed that fairly high contents of this metal ($> 30 \cdot 10^{-6}\%$) are fairly typical of the sandy bottoms of shallow-water active zones south of Whale Island. However, these values are 20 times less than those found in soil in the terrestrial part of the island's thermal field. Analysis for mercury in clayey, deeper-water sediments brought up in an area of underwater drilling near Whale Island reveal that the content of Hg at the seafloor in this area (an active zone) is higher than in neighboring inactive areas of the seafloor; mercury measurements $100 \cdot 10^{-6}$ and $10 \cdot 10^{-6}\%$ respectively. The latter value is evidently typical of background values for the region. Maximum concentrations of mercury were found in sediment infilling sulfur and sulfur-sulfide gas channels penetrating high-temperature mud at the bottom of the sink (more than $500 \cdot 10^{-6}\%$).

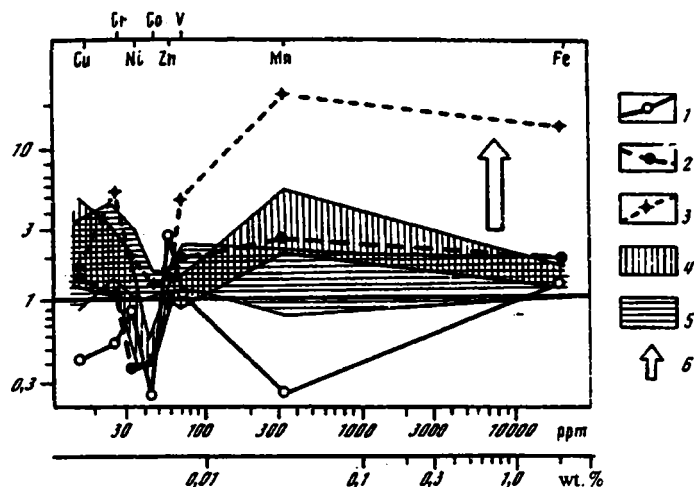


Fig. 3. Abundances of chemical elements in various types of marine bottom sediments in the southern part of the Bay of Plenty. The positions of symbols and fields correspond to rock compositions normalized to the composition of "non-enriched" sediment [12]. 1-3) Trend of composition (1 – hydrothermal clays of the Calypso zone [20]; 2 – andesitic greywackes of the North Island axial ridge, New Zealand [11]; 3 – finely dispersed colloidal material precipitated at a geochemical barrier, a "sea water-acidic streamlet" near White Island [12]); 4-5) composition fields of bottom sediments in the Bay of Plenty (4 – according to data from the 30th cruise of the R/V *Vulkanolog*, 5 – according to [14]); 6) direction of relative increase in compositions of chemical elements in bottom sediments.

The content of Hg in sediments of the Calypso zone is generally an order of magnitude greater than the concentrations of this metal in the bottom soils of other active areas of seafloor in the region. It is lower than that found in the investigated portion of the thermal field near Whale Island. This does not apply to hydrothermal clays composing the gryphons which discharges pass through in the Calypso zone. Anomalously high ($89.5 \cdot 10^{-4}\%$) concentrations of mercury have been found in these deposits [19]. The comparatively low contents of mercury in the majority of bottom sediments in the Calypso zone does not indicate less activity in this area of the seafloor, since the rate of mercury influx from the depths of the Earth is not the only important process regulating the concentration of this metal at the surface. The environment and the physical-chemical properties of the sink-collectors play a major role here. The distribution of mercury in bottom and terrestrial sediments in the investigated zone is shown in a generalized scheme (Fig. 4).

GAS- AND HYDROCHEMICAL INVESTIGATIONS

Abundances of metals, both dissolved in seawater and occurring in suspension, are typical of the Bay of Plenty, especially the part of the Bay of Plenty located in the vicinity of White and Whale islands (Table 3). This is probably a consequence of widespread present-day hydrothermal activity in the area. However, the same cannot be said of all elements. Surprisingly low concentrations of manganese were found [3]; this is unusual, since hundred- or thousand-times higher concentrations of manganese are ubiquitous in other known regions of present-day hydrothermal activity [16].

From our point of view, there is an interesting phenomenon in the present-day zone of hydrothermal discharge south of Whale Island, where the abundance of suspended matter is significantly greater than in the surrounding waters of the Bay of Plenty. Here, maximum concentrations are found at the surface rather than in the near-bottom layer. This could be a result of intensive development of plankton or a flotation effect when suspended particles are carried to the surface by gas bubbles. The similar ratios of concentrations of the considered elements in suspension over the entire length of the water column at a given point is evidence in support of the latter possibility.

Discrete hydrochemical sampling in the vicinity of the Calypso zone was carried out along a traverse crossing the zone in a sublatitudinal direction (see Fig. 1). Based on the analysis of the samples from different horizons of the water column, we constructed hydrochemical profiles characterizing the distribution of a number of parameters and chemical

TABLE 3. Abundances of Metals in Seawater in the Southern Part of the Bay of Plenty, mm/liter

Station no.	Horizon, m	Fe	Mn	Cu	Zn
39	280	3,4/8,5	0,30/0,07	0,22/2,63	0,24/22,13
50	180	2,6/1,5	0,09/0,08	0,17/0,38	0,43/7,38
	205	2,6/2,0	0,13/0,11	0,44/2,00	0,38/18,13
49	90	18,0/30,8	0,50/0,09	0,93/4,12	1,90/30,50
	140	3,7/8,5	0,05/0,04	0,21/2,63	0,40/22,13
	160	4,8/15,25	0,17/0,07	0,26/2,13	0,52/38,25
	180	3,3/11,06	0,22/0,08	0,39/3,07	1,23/55,75
51	150	1,6/12,12	0,22/0,07	0,22/1,75	0,37/21,25
53	170	3,7/5,12	0,16/0,25	0,13/1,38	0,47/20,75
54	275	2,8/9,75	0,11/0,15	0,28/1,35	1,33/23,75
60	25	3,3/4,75	0,07/0,15	0,18/1,12	0,52/24,00
36/2	0	8,0/10,8	0,16/0,22	0,28/3,25	0,68/12,50
	40	8,0/3,5	0,24/0,25	0,24/3,38	1,14/9,25
	90	13,0/7,0	0,28/0,29	0,32/5,21	0,96/43,25
70	0	68,8/19,1	1,32/0,31	2,60/10,87	6,70/72,90
	30	21,9/14,25	0,47/0,15	0,78/2,21	2,50/42,90
	45	31,6/25,0	0,72/0,25	0,94/5,38	3,20/52,50
Seawater		1,0/5,0	0,03/0,40	0,12/1,40	0,30/5,00
Whale Island (spring source)		—/69100	—/160	—/180	—/240
White Island (streamlet)		—/83200	—/2700	—/800	—/1040

Explanation. 1. The suspended phase is shown in the numerator and the dissolved phase is shown in the denominator. 2. Analysis of seawater samples was carried out with preparative concentration. Quantitative determinations were performed by atomic absorption at the Central Chemical Laboratory of the Institute of Volcanology, Far-East Branch of the Academy of Sciences of the USSR (Petropavlovsk-Kamchatskii). N. A. Tyurina.

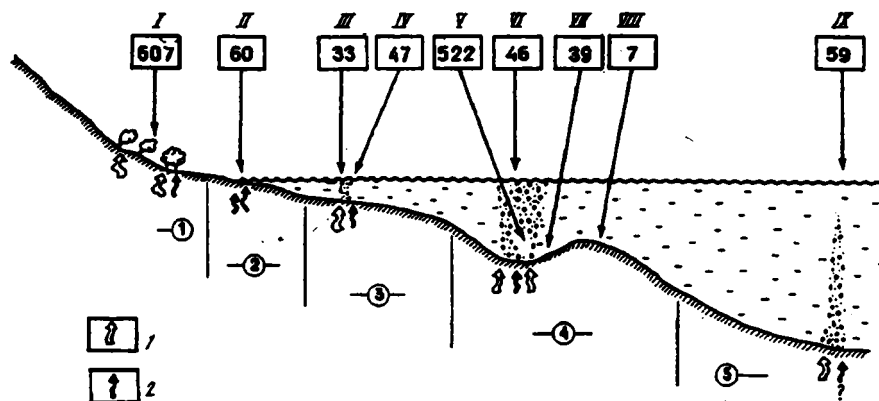


Fig. 4. Content of mercury in sediments in different segments of a schematic section of Whale Island, the present-day Calypso zone of hydrothermal activity. Mercury concentrations are given in terms of $n \cdot 10^{-6}\%$ (N. Ya. Mochalina, analytical chemist). I) Soil from terrestrial thermal area on Whale Island; II) sand from littoral part of thermal area; III) sand from depth of 10-12 m on the southern underwater slope of Whale Island; IV) sandy titanomagnetite aggregates cemented with sulfides; V) mud from inner belt of sulfurous gas channels of an active sink near Whale Island; VI) mud from active zone of sink; VII) mud from inactive outer slopes of sink; VIII) soil from within active zone of sink; IX) mud from active Calypso zone; 1-2) vents (1 — gas; 2 — thermal). For explanations of other symbols, see Fig. 1.

constituents. The most indicative of these are shown in Fig. 5. In terms of salinity values (see Fig. 5a) the seawater is fairly well stratified to depths of 120-130 m; however, in terms of pH values (see Fig. 5b) stratification cannot be traced at these depths. Downward along the profile, both these parameters begin to decrease, reaching minimal values within a relatively

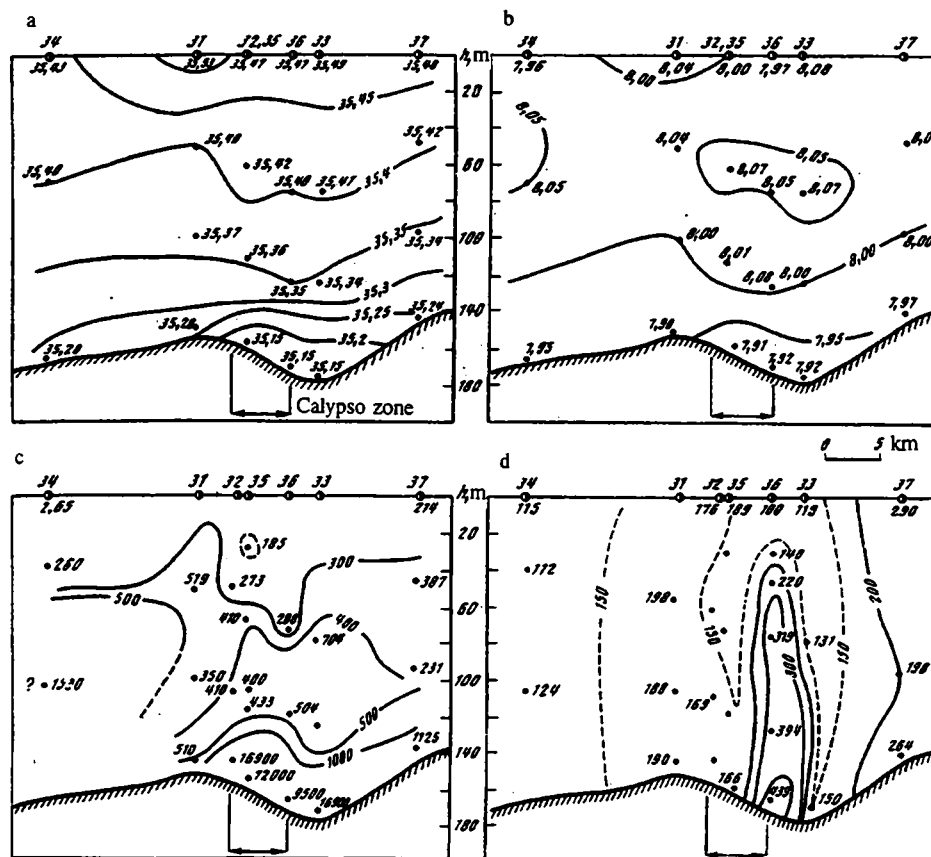


Fig. 5. Distribution of hydrochemical parameters along a vertical profile through the present-day Calypso hydrothermal zone. The data presented were obtained by discrete hydrochemical sampling of horizons of the water column (see Fig. 1 for the location of the profile). a) Salinity, ‰; b) pH; c) methane CH_4 , $\text{n} \cdot 10^{-6}$ vol.%; d) carbon dioxide CO_2 , $\text{n} \cdot 10^{-3}$ vol. %.

local area coinciding in plan with the active Calypso zone. It is evident that this distribution pattern of salinity and pH is due to present-day hydrothermal activity resulting in freshening (due to the fresh-water nature of the thermal solutions [15]) of water and a decrease in pH of waters adjacent to the active zone.

Evidence of this includes the distribution of dissolved gases in the hydrochemical profiles under consideration. Methane and carbon dioxide are most telling in this regard (see Fig. 5c, d). Methane forms a near-bottom anomaly exceeding background values by one-two orders of magnitude, whereas CO_2 forms a "tongue" of anomalous concentrations extending from the bottom almost to the surface of the water column and exceeding background values several times over. An increase in the concentration of CO_2 will decrease the pH in the water. Without any doubt, the elevated contents of these gases in the seawater are a result of present-day hydrothermal activity in the Calypso zone; as mentioned above, this is reflected in the values of other parameters in the environment.

* * *

Investigations carried out during the 30th cruise of the R/V *Vulkanolog* and the 18th cruise of the R/V *Akademik Nesmeyanov* allowed us to refine previously obtained data and allowed us to obtain new data concerning the layout of the present-day zone of hydrothermal activity in the southern part of the Bay of Plenty, the compositions of its constituent formations, and details of the hydrothermal process. Our principal conclusions can be formulated as follows.

1. Geophysical methods reveal that hydrothermal discharges at the seafloor are confined to a tectonically isolated zone which is a seaward continuation of the region of active Taupo-Rotorua volcanism on land. Structural features of the

sedimentary cover in the zone investigated include: partially eroded folds, aprons of volcanoclastic rock and gas-saturated sediments, a large number of faults.

2. The sedimentary formations occurring in the zone of present-day manifestation of hydrothermal activity are mainly products of the erosion of andesitic greywackies of Mesozoic age from axial ridges of North Island. We found evidence supporting previous conclusions that there is no substantial regional enrichment of these sediments with metals during present-day hydrothermal activity.

3. The ore mineralization in the upper part of the sedimentary section primarily consists of several types of sulfide formations. The origin of these formations was associated with metasomatic conversions of primary magnetite during seepage of hydrogen sulfide through magnetite-bearing sand.

4. Essentially hydrothermal formations were discovered in zones of direct discharge of submarine thermal springs. They differ from monotypic sediments with regard to temperature, physical-chemical parameters, H_2S saturation, and behavior of mobile metallic species.

5. Gas- and hydrochemical investigations reveal a lack of contrasting local anomalies in the water column of the region with respect to the parameters measured. Methane and carbon dioxide dissolved in the water and forming "tongues" of anomalous concentrations at vents of submarine thermal springs constitute an exception. This confirms the predominantly gaseous character of the present-day hydrothermal activity in the region.

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CHEMISTRY OF BASALTS, Fe–Mn-NODULES AND CRUSTS FROM SEAMOUNTS IN THE NORTHWESTERN PART OF THE PACIFIC OCEAN

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A comparative analysis of the material composition of basaltic rocks, Fe–Mn nodules, and crusts from submarine mountains in the northwestern part of the Pacific Ocean (the Castor and Pollux guyots and the Magellan Mountains) reveals similar chemical features of basalts and the Fe–Mn-formations spatially associated with them. We propose that there is a genetic connection between nodules (crusts) and local basalt substrate as a result of participation in the formation of nodules and crusts by a number of elements supplied from basalts during their halmyrolysis in near-bottom waters and sediments to the material composing hydrogene Fe–Mn-formations.

In 1988, during the 13th cruise of the R/V *Akademik Aleksandr Nesmeyanov* under the leadership of B. I. Vasil'ev (Pacific Ocean Institute, Academy of Sciences of the USSR), we carried out special dredgings of the Castor (25°39'–25°53' N, 146°44'–147°09' E) and Pollux (25°34'–25°51' N, 147°34'–147°46' E) guyots and the Magellan Mountains (16°57'–18°04' N, 150°23'–152°22' E) in the northwestern part of the Pacific Ocean (Fig. 1). We brought up fragments of igneous and sedimentary rock as well as Fe–Mn-nodules and crusts from the slopes of seamounts at depth intervals of 5440–1040 m.

On the basis of these data, it is reasonable to reconsider the relationship between the composition of Fe–Mn-nodules and crusts and the composition of the basaltic substrate on which these crusts or sediments with nodules are formed. The dominant view that the formation of nodules and crusts is a consequence of supplies of components from ocean water, pore solutions, and bottom sediments [1, 4, 12, 13, 17], together with the lack of apparent correlation between the compositions of nodules (crusts) and rocks of the solid oceanic crust, give reason to suppose that a correlation will be found primarily with basalts of ocean floor [16].

Evidence in favor of this view includes data on the efflux of such ore components of nodules and crusts as Mn, Cu, and Zn [8] during circulation of sea water as well as the slow growth rates of concretions and nodules, averaging 2–4 mm/10⁶ yr [1]. These rates would permit migration of petrogenic and ore elements from ocean-floor basalts altered by underwater erosion [6, 11] into overlying sediments and near-bottom waters and, from there, into nodules and crusts.

The role of basaltic ocean-basement rock as a source of material for Fe–Mn-nodules and crusts is supported by data on coincidence of fields of Fe–Mn-nodules and areas of highly ferruginous basalts [2, 5, 7, 8], confinement of nodules and crusts with Co and Pt to guyots with volcanic edifices containing picrite-basalt complexes rich in Ni, Co, and Pt [2], and elevated contents of Ni, Co, and Pt in the lower parts of crusts on rocks composing guyots [1, 14, 17].

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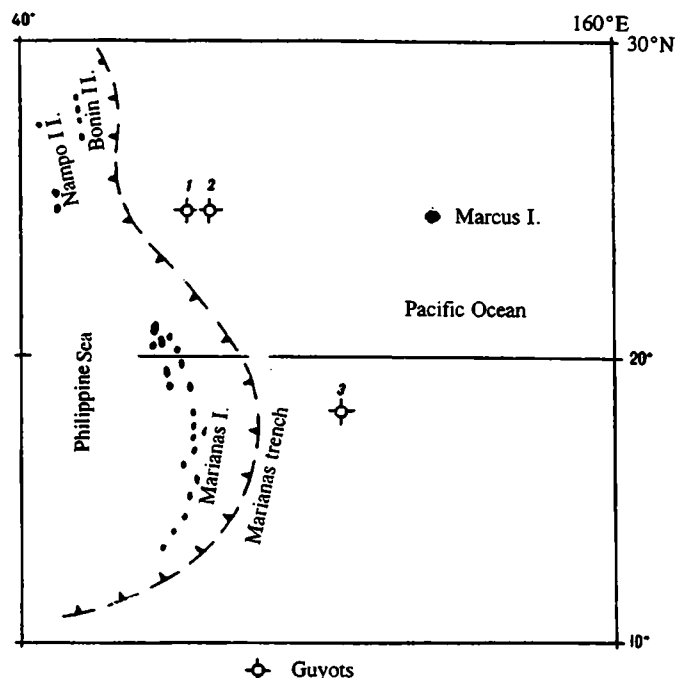


Fig. 1. Map showing positions of seamounts investigated. 1) Pollux Guyot; 2) Castor Guyot; 3) Magellan Mountains.

Monotypic values and variations in certain chemical parameters of basalts and nodules and crusts spatially associated with basalts are the most persuasive evidence for a direct connection between the composition of a basalt in a specific area, the morphostructure of the ocean floor, and the Fe—Mn-nodules and crusts occurring there. To find values of these chemical parameters, we carried out a multisided comparative analysis of the material composition of basaltic rocks as well as Fe—Mn-nodules and crusts from seamounts in the northwestern part of the Pacific Ocean. The results of this analysis are presented in the following sections of this report.

PETROGRAPHY AND PETROCHEMISTRY OF BASALTIC ROCKS FROM SEAMOUNTS

The associations of basaltic rock found on the Castor Seamount, the Pollux Seamount, and the Magellan Mountains are similar in overall mineral-species composition, although they differ with respect to certain petrographic and petrochemical features. It is evident that the existence of analogous features in the compositions of Fe—Mn-nodules and crusts on the corresponding submarine rises favor a role for ocean-floor basalts as sources of material for Fe—Mn-nodules. For this reason, separate descriptions of petrography and petrochemistry of basaltic rock on seamounts will be given for the Castor Seamount, the Pollux Seamount, and the Magellan Mountains.

Basaltic Rocks of the Castor and Pollux Seamounts. Sampling of the slopes of these two submarine rises was carried out over a depth range of 4700-1700 m; samples of picrite and picrobasalts, ankaramitic, olivine, plagioclase-porphyry, and aphyric basalts and trachybasalts were obtained as a result. Despite wide variations in quantitative-mineralogical composition, structure, and texture, all of the enumerated rocks are characterized by consistent presence of olivine, phenocrysts of rock-forming minerals, a vitreous or cryptocrystalline mesostasis, and amygdaloidal varieties. The commonality of the main characteristics of some of the basaltic rocks of the Castor and Pollux guyots and the possibility of representing the compositions of such rocks in the form of a series of differentiates of a single melt justifies group description of these rocks.

The picrite, picrobasaltic, olivine, and aphyric basalt group includes rocks with olivine content ranging from 15-60% in picrites and picrobasalts to 1-5% in aphyric basalts. Only olivine, in addition to being present in the rock matrix, is present in substantial quantities in the form of phenocrysts up to 1-3 mm in size. The content of plagioclase in the form of laths up to 0.08×0.6 mm in size equals 10 to 60% (depending upon the degree of recrystallization of the rock); in terms of compo-

TABLE 1. Composition of Rock-Forming Minerals in Basalts of Seamounts, wt. %

Component	Castor guyot									Castor guyot				Magellan Mts.			
	plagioclase					monoclinic pyroxene				olivine	ore mineral			plagioclase		monoclinic pyroxene	
	12/1	18/5	15/4	13-ya	13/1-k	12/1	18/5	15/4-ya	15/4-ya	12/1	12/1	18/5	13/1	77/26-c	77/26	77/26-ya	77/26-k
SiO ₂	50,5	51,66	50,76	50,39	54,29	51,93	44,46	49,58	45,15	39,83	0,90	1,39	1,33	50,22	52,85	46,76	51,08
TiO ₂	0,08	0,08	0,10	0,08	0,18	1,65	3,25	1,43	4,45	—	46,77	22,28	28,62	0,07	0,23	2,67	1,20
Al ₂ O ₃	30,81	30,56	31,85	29,58	29,50	3,70	7,28	4,91	9,34	—	0,36	2,66	2,12	32,11	30,37	8,05	4,88
FeO	0,67	0,77	0,88	0,39	0,97	9,96	14,43	5,66	8,61	9,82	49,13	70,45 *	61,57 *	0,41	0,82	7,76	6,56
MnO	—	—	—	—	—	0,22	0,23	0,12	0,15	0,17	0,46	0,63	0,66	—	—	0,15	0,15
MgO	0,23	0,23	0,05	0,10	0,10	13,26	9,77	14,36	10,79	47,83	2,54	0,91	1,38	—	0,03	12,48	14,64
CaO	13,93	13,91	14,42	13,16	12,73	19,40	20,62	21,94	21,91	0,27	0,17	0,35	0,28	14,86	12,98	20,94	21,10
Na ₂ O	4,02	3,45	3,33	4,30	4,93	0,34	0,42	0,31	0,51	—	—	—	—	3,10	4,15	0,44	0,34
K ₂ O	0,05	0,04	0,22	0,11	0,14	—	—	—	—	—	—	—	—	0,08	0,23	—	—
Cr ₂ O ₃	—	—	—	—	—	0,20	0,15	0,48	—	0,15	—	0,10	0,10	—	—	0,41	0,25
NiO	—	—	—	—	—	—	—	—	—	0,39	—	—	—	—	—	—	—
Total	100,29	100,70	101,61	98,11	102,84	100,66	100,73	98,79	100,91	98,46	100,33	99,11	96,06	100,85	101,66	99,66	100,20
An	66,1	69,3	70,1	62,8	58,6	—	—	—	—	—	—	—	—	72,2	62,6	—	—
Or	0,3	0,2	1,2	0,6	0,8	—	—	—	—	—	—	—	—	0,5	1,3	—	—
En	—	—	—	—	—	37,3	28,7	45,0	29,9	—	—	—	—	—	—	37,2	42,5
Wo	—	—	—	—	—	40,1	44,9	40,6	45,5	—	—	—	—	—	—	45,8	44,9
Fs	—	—	—	—	—	—	—	—	—	89,6	—	—	—	—	—	—	—
Name	Labradorite					Augite	Sahlite	Augite	Sahlite	Chrysolite	Ilmenite	Titanomagnetite		Bytownite	Labradorite	Sahlite	

Explanation. Rocks of normal alkalinity: 12/1) picrite; 18/5) aphyric basalt. Rocks of elevated alkalinity: 15/4) ankaramitic basalt; 77/26) plagioclase-porphyry basalt. 13/1) trachybasalt. Letters following sample numbers indicate: c) phenocryst; ya) nucleus; k) edge. Analyses carried out by G. N. Muravitska using a "Kameka MS-46microprobe.

*Iron content in the form of Fe₃O₄.

sition, this is laboradorite An_{69-66} containing a 0.2-0.3% orthoclase component (Table 1). Corroded plagioclase phenocrysts up to 0.7×1.2 mm in size occur in the form of isolated grains. Monoclinic pyroxene, colorless or brownish, is represented by augite $Wo_{40}En_{37}Fs_{23}$ in picrite and by sahlite $Wo_{45}En_{29}Fs_{26}$ in aphyric basalt (see Table 1) and is present in quantities of up to 10-40% in the form of grains up to 1 mm in size. An ore mineral (ilmenite or titanomagnetite) is present in quantities of 2 to 10% in the form of isolations up to hundredths of a millimeter in size. A vitreous and cryptocrystalline mesostasis makes up from 3 to 40% of the rock volume. The secondary minerals are: smectite, iddingsite, bowlingite, chlorophoeite, serpentine, talc, chlorite, and calcite. The texture of the basalt ranges from hyalopilitic and intersertal to ophitic and poikilophitic. In the case of an amygdaloidal texture, the quantity of amygdules reaches 50% and the sizes of amygdules reach 5 mm. Amygdules contain smectite, zeolites, and calcite.

The petrochemical parameters of the rocks in the group being described (Table 2) indicates that they are basites of a normal range of alkalinity belonging to the potassium-sodium series. Their genetic affinity and formation as a result of differentiation of a single parental magma is suggested by progressive increases in these parameters in the order picrite—olivine basalt—aphyric basalt. These parameters include: total iron indices $FeO'/(FeO' + MgO)$ equal to 0.30, 0.41, and 0.57; alumina indices $Al_2O_3/(Fe_2O_3 + FeO + MgO)$ equal to 0.18, 0.38, and 0.75; decreasing Na/K ratios (4.0; 3.7; 3.1) and Ni/Co ratios (14.2; 8.7; 4.7). Based on the value of these such parameters as Ti/V, equal to 38-55, picrites as well as olivine and aphyric basalts of the Castor and Pollux guyots correspond to ocean-floor basalts and varieties transitional to basalts of oceanic islands [18].

The group of ankaramitic basalts, plagioclase-porphyry basalts, and trachybasalts show the following indications of belonging to the subalkaline rock series: elevated content of the orthoclase component in plagioclases; character of monoclinic pyroxene represented by sahlite and titanaugite.

The ankaramitic basalts are melanocratic rocks consisting of 10-20% plagioclase (labradorite—bytownite $An_{70}Or_{1-2}$), 40-60% lilac-brown monoclinic pyroxene (augite—sahlite $Wo_{41-45}En_{45-30}Fs_{14-25}$) in the form of 0.03-0.15 mm grains in the rock matrix and phenocrysts up to 0.2×0.4 mm in size, from 5 to 20% olivine contained in the groundmass of the rock in the form of 0.1×0.2 -mm segregations, and phenocrysts (up to 0.5×0.8 mm in size) of an ore mineral in concentrations of 3-8%, with segregations hundredths of a millimeter in size. The presence of a vitreous and cryptocrystalline mesostasis in quantities of 15-25% has given the rock an intersertal texture. The structure is massive, occasionally amygdaloidal. The content of amygdules is up to 15%; amygdules are up to 0.6 mm in size and are filled with chlorite and calcite.

The plagioclase-porphyry basalts and trachybasalts are distinguished from the ankaramitic basalts by higher content of plagioclase (from 30 to 65%) represented by labradorite $An_{63-59}Or_{0.6-0.8}$, which is present in the form of 0.03×0.4 -mm laths in the groundmass of the rock and phenocrysts up to 0.7×1.5 mm in size. The content of colorless and brownish monoclinic pyroxene ranges from 10 to 30%; segregations of this mineral are up to 0.4×0.5 mm in size. Olivine is present in the rocks being described in quantities ranging from 1 to 15% in the form of grains up to 0.3×0.8 mm in size. A characteristic feature of the plagioclase-porphyry basalts and trachybasalts, in addition to high plagioclase content, is enrichment (8-12%) with titanomagnetite ($TiO_2 = 29\%$) in the form of 0.02-0.1-mm segregations. The rocks are also distinguished by substantial content a vitreous base (from 15 to 70%), trachytoid character, and amygdaloidal texture. The abundance of amygdules is 20-30%; they are up to 1-3 mm in size.

Analysis of the distribution of the above-described rocks with respect to depth of occurrence on guyots reveals that picrite and picrobasalt, olivine, plagioclase-porphyry, and aphyric basalt occur in the interval from 4700 to 3500-3000 m. Higher, in the interval of 2900-1700 m, there are ankaramitic, olivine, and plagioclase-porphyry basalts; in the interval of 2000-1700 m, there are only ankaramitic and olivine basalts.

Basaltic Rocks of the Magellan Mts. Dredgings of two submarine rises in the depth interval of 5440-1730 m yielded fragments of picrobasalt, ankaramitic, olivine, olivine-pyroxene-plagioclase-porphyry, pyroxene-plagioclase-porphyry, plagioclase-porphyry, and aphyric basalts as well as trachybasalts. The rocks listed are composed of the same minerals but differ in abundances of minerals and variations in compositions of minerals as well as structure and texture. This allows us consider the rocks of the Magellan Mts. as a series of differentiates of a single parental magma. The rocks of the series can be subdivided into several groups on the basis of specific quantitative-mineral and structural characteristics.

The picrobasalt, ankaramitic, and olivine-basalt group are distinguished by high content of olivine, with olivine present in the composition of the matrix as well as in the form of phenocrysts up to 2 mm in size accompanied by massive, very fine-grained structure of picrobasalt and ankaramitic basalt. Picrobasalts contain 15-20 vol.% olivine phenocrysts which occur in a microlithic base containing 15-20% plagioclase segregations. In comparison to picrobasalts, ankaramitic basalts contain less olivine (10-20%), plagioclase (10-20%), and much more (50-65%) brownish-lilac monoclinic pyroxene in the

TABLE 2. Chemical Composition of Basalts of Seamounts

Constituent	Castor Guyot			Magellan Mts.						
	12/1	12/9	18/5	76/1	77/26	85/10	100/1	N-1	N-2	N/2-1
SiO ₂	40,9	43,20	46,00	43,00	45,70	39,80	45,80	48,53	45,37	49,49
TiO ₂	0,80	1,53	1,41	3,83	2,34	3,43	2,93	2,33	2,24	2,69
Al ₂ O ₃	6,80	10,50	15,05	15,44	16,75	13,0	17,50	15,33	16,05	16,73
Fe ₂ O ₃	5,32	8,21	8,54	12,93	7,98	9,39	10,26	5,17	9,27	3,41
FeO	6,37	3,64	3,25	3,08	3,39	3,29	0,67	3,57	2,05	4,87
MnO	0,17	0,16	0,15	0,19	0,14	0,15	0,087	0,18	0,09	0,04
MgO	26,20	15,50	8,21	2,48	4,59	6,82	2,14	6,03	2,68	2,82
CaO	5,45	7,50	8,56	7,10	10,84	11,90	7,74	7,48	8,89	8,08
Na ₂ O	1,21	1,83	2,59	3,63	3,37	1,87	3,79	3,07	3,86	3,13
K ₂ O	0,23	0,49	0,84	1,46	0,88	1,08	1,33	1,74	2,32	2,17
H ₂ O ⁻	1,00	2,18	2,45	2,99	1,90	3,49	3,25	0,98	1,12	1,44
H ₂ O ⁺	4,24	4,52	2,57	2,41	1,03	3,19	2,00	3,78	3,56	2,76
P ₂ O ₅	0,094	0,18	0,14	0,87	0,39	1,79	1,63	1,25	1,94	1,77
CO ₂	0,76	0,07	0,06	0,10	0,11	0,14	0,19	—	—	—
Total	99,54	99,51	99,82	99,51	99,41	99,34	99,32	99,44	99,44	99,39
Sr	65	120	154	513	436	1025	513	Not det.	Not det.	Not det.
Ba	21	37	46	314	197	421	269	•	•	•
Lj	34	74	79	29	46	74	31	•	•	•
Rb	9	12	19	22	16	15	26	•	•	•
Ni	1336	581	322	37	79	236	55	152	130	83
Co	94	67	68	29	35	51	24	40	15	18
Cu	67	78	120	160	61	136	136	67	94	67
Zn	96	96	257	297	128	321	209	95	91	76
Pb	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	Not det.	59	19	22

Explanation. Rocks of normal alkalinity: 12/1) picrite; basalts: 12/9) olivine, 18/5) aphyric. Rocks of elevated alkalinity: 76/1) trachybasalt; basalts: 77/26) plagioclase-porphyry, 85/10) olivine, 101/1 and N-1) olivine-plagioclase-porphyry, N-2) olivine-plagioclase-porphyry, N-2/1) plagioclase-porphyry. Samples 12/1, 12/9, 76/1, 77/26, 85/10, and 100/1 from the collection of Yu. I. Dmitriev. Analytical chemist: Yu. V. Dolinina; analyses H-1, H-2, and H-2/1 were taken from [5].

Oxide content is given in wt. %; element abundances are given in g/tons.

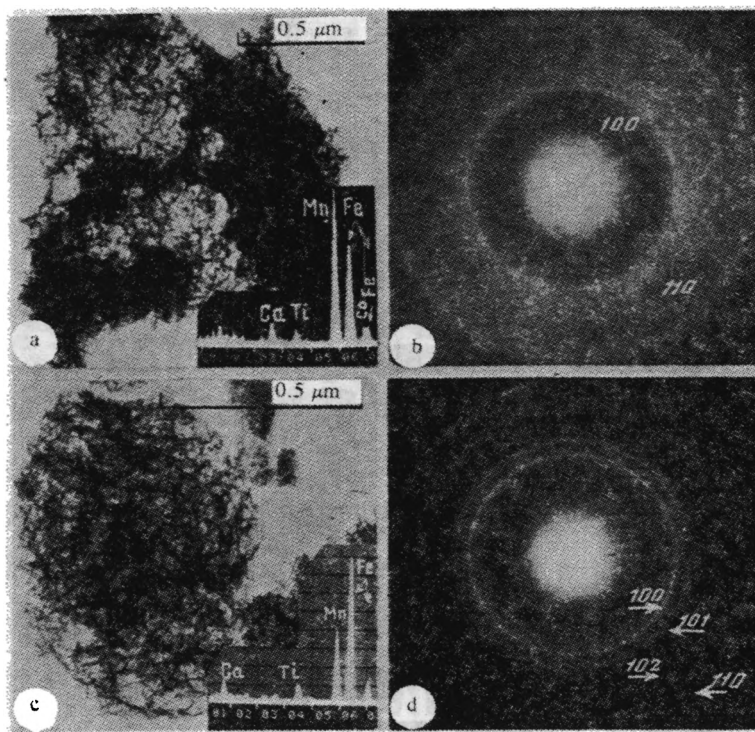


Fig. 2. Electron photomicrograph of aggregates of Fe-vernadite (a) and Mn-feroxyhyte (c); in insets) energy distribution spectra of these minerals; b, d) electron diffraction patterns of aggregates of the Fe-vernadite and Mn-feroxyhyte respectively.

form of very small (0.02-0.06 mm) segregations in the rock matrix and sparse phenocrysts measuring up to 0.6 mm. Ore mineral is present in the base of the rock in quantities of 5-8%. Olivine basalts contain 5-15% olivine, up to 55% plagioclase, and 20-40% monoclinic pyroxene; they are distinguished by the presence of glass in the mesostasis, trachytoid structure in many cases, and, in some cases, amygdules up to 2 mm in size in quantities ranging from 2 to 40%. Secondary minerals in picrobasalt, ankaramitic basalt, and olivine basalt include: serpentine, iddingsite, smectite, talc, chlorite, calcite, and goethite.

The group including olivine-pyroxene-plagioclase-porphyry, olivine-plagioclase-porphyry, pyroxene-plagioclase-porphyry, and plagioclase-porphyry basalts is characterized by low (less than 5%) olivine content or almost complete absence of olivine as well as persistent presence and predominance of plagioclase among phenocrysts. Trachytoidal and amygdaloidal structures are typical of rocks in this group. Zoned and corroded phenocrysts of plagioclase (bytownite An_{72} , see Table 1) with inclusions of glass and vitreous fringes are up to 2×9 mm in size and are present in quantities of up to 20%. Phenocrysts of olivine are also occasionally corroded, contain inclusions of glass, reach dimensions of 2×4 mm, and are present in quantities ranging between 1 and 5%. Early segregations of monoclinic pyroxene in olivine-pyroxene-plagioclase-porphyry basalts occur in quantities ranging from 1 to 5% and measure up to 0.7×0.9 mm. The matrix of a basalt in this group consists of plagioclase (labradorite An_{63} , see Table 1) in amounts ranging from 10 to 60%, up to 35% lilac-brown monoclinic pyroxene (sahlite $Wo_{46-45}En_{42-37}Fs_{22-18}$, see Table 1), 5-8% ore mineral, and up to 60% vitreous and cryptocrystalline mesostasis. Mineral segregations in a basis of basalt range from hundredths to tenths of millimeters in size. Secondary minerals within the composition of the rock include: serpentine, smectite, chlorite, palagonite, and goethite.

The basalt and trachybasalt group are represented by rocks which are almost aphyric and devoid of olivine, with the exception of occasional grains of this mineral in trachybasalts. Corroded microphenocrysts up to 0.2 mm in size with glass inclusions occur here in quantities of 1-2%. The matrix of this rock consists of up to 60% laths of plagioclase (up to 0.1×0.7 mm in size), 30-35% monoclinic pyroxene (up to 0.3×0.5 mm in size), ore mineral in the form of grains (0.05 mm in size, up to 5% in basalts and up to 15% in trachybasalts), and a vitreous mesostasis which confers hyalopilitic, pilotaxitic, and intersertal textures upon the base of basalt and trachybasalt. The structure of the rock is massive and amygdaloidal.

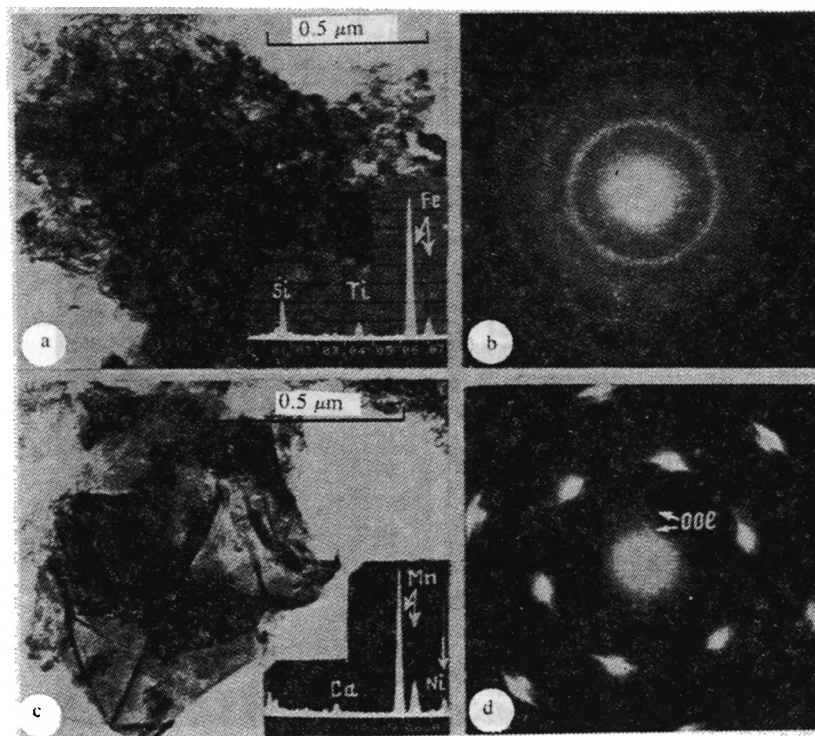


Fig. 3. Electron photomicrograph of Fe-x-mineral (a) an asbolane-buzerite (c); in inserts: their energy-dispersion spectra; electron diffraction patterns from finely dispersed aggregates of Fe-x-mineral (b) and flake of asbolane-buzerite (d).

A number of petrographic features of the rocks of the Magellan Mts. indicate that the rocks are of elevated alkalinity. These include elevated content of the orthoclase constituent in plagioclase, membership of the monoclinic pyroxene to the sahlite group (see Table 1), and the frequent occurrence of trachytoid structure. Chemical analyses of the basaltic rocks of the Magellan Mts. (see Table 2) recalculated to water-free composition and plotted on a silica-alkali classification diagram suggest classification of these rocks as subalkaline basites. Other petrochemical and geochemical parameters suggest that these are moderately high-alumina rocks, $\text{Al}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{FeO} + \text{MgO}) = 0.7\text{-}1.5$, and a potassium-sodium series with $\text{Na}_2\text{O}/\text{K}_2\text{O} = 1\text{-}4$ and a total iron index $\text{FeO}'/(\text{FeO}' + \text{MgO})$ ranging from 0.6 in olivine and olivine-bearing basalts to 0.9 in trachybasalts. The formational classification of volcanic rocks of the Magellan Mts. as ocean-island basalts is determined both by the geological setting of the rocks and the high (70-150) ratios of titanium to vanadium [18].

The hypsometric positions of samples of effusive rock brought up from the slopes of the Magellan Mts. most likely do not reflect original positions in sections of submarine volcanoes. It can be assumed, however, that basalts located at the feet of slope of these morphostructures and occurring at higher levels belong to earlier stages of volcanic activity. Accordingly, basalts that can be traced along the slopes of a rise to minimal depths are most likely very young formations. If, based upon these observations, we assess the eruption sequence of basalts in the Magellan Mts., the oldest member of the basite formation here should be classified as trachybasalt, found at depths from 5400 to 4000 m, and the youngest member should be classified as picrobasalt and olivine picrobasalt, found at depths of 2800-2600 m. The evolution of the magmatism from less alkaline to more alkaline rocks (an antidromal trend) is a result of drainage of vertically differentiated chambers and is typical of oceanic-island volcanism [10].

When the material and structural characteristics of basaltic rocks from the submarine rises of the two study areas are compared, one can easily see the appreciable basicity and melanocratic character of the basite association of the Castor and Pollux guyots, in which picrite and picrobasalt play a substantially greater role than in the association in the Magellan Mts.; monotypic rocks typically containing more olivine and, accordingly, magnesium and nickel. Another feature distinguishing the basites of the Castor and Pollux guyots from the basites of the Magellan Mts. is widespread occurrence of amygdaloidal varieties among the former; this suggests occurrence of the effusive process in relatively shallow water.

TABLE 3. Chemical Compositions of Fe–Mn-Nodules and Crusts

Element	Pollux Guyot			Castor Guyot				Magellan Mts.		
	7/5	7/5a	7/5b	20/12	20/12a	20/12b	20/12c	101	101a	101b
Al	0,19	0,25	0,48	0,30	0,20	0,74	0,38	0,58	0,84	0,73
Fe	6,06	10,12	10,89	8,32	8,57	16,2	13,58	11,63	14,90	14,48
Mn	31,06	26,39	28,31	28,31	28,27	17,86	19,40	21,81	17,77	17,21
Mg	1,36	1,02	1,07	1,29	1,13	0,90	0,87	0,86	0,88	0,94
Ca	2,47	2,14	2,11	1,82	1,83	1,62	1,72	3,65	1,99	2,88
Na	1,70	1,62	1,59	1,85	1,82	1,69	1,66	1,61	1,38	1,31
K	0,61	0,41	0,41	0,50	0,47	0,41	0,35	0,40	0,38	0,38
Sr	1200	1300	1300	1200	1300	1200	1400	1500	1300	1300
Ba	1700	1400	880	1700	1600	1200	990	2400	1200	1100
Li	2,3	1,7	3,8	4,3	1,2	1,7	1,4	2,9	4,3	6,0
Rb	3,5	0,9	1,7	2,4	≤ 1,1	2,1	0,9	2,4	2,4	4,4
Ni	10800	6300	5500	10500	8800	3400	4100	4600	3400	3500
Co	9200	6100	12100	9600	8400	6300	8600	4300	5800	5500
Cr	76	64	58	63	72	34	36	34	26	43
Cu	790	600	190	1900	2300	690	250	1900	1000	770
Zn	1300	640	710	970	850	540	550	690	600	650
Pb	1900	1900	1700	1500	1500	1400	1500	1400	1300	1300

Explanation. 7/5-7/5b) nodules with phosphorite core; 7/5) core, 7/5a) zone 2 (3 mm from surface), 7/5b) surface layer; 20/12-20/12c) crust on limestone: 20/12) lower part, 20/12a-20/12c upper part; 101-101b) nodule (101 core, 101a middle portion, 101b surface layer). Contents of Al, Fe, Mn, Mg, Ca, Na, and K are given in wt. %; other elements are given in g/ton.

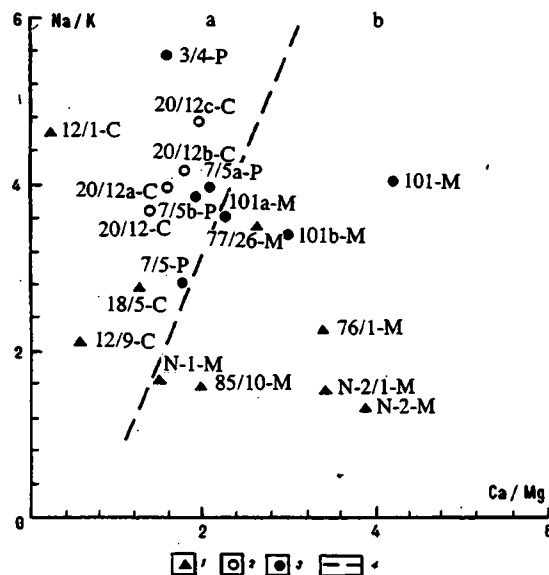


Fig. 4. Compositions of basalts, Fe-Mn-nodules and crusts in Na/K-Ca/Mg coordinates: 1) basalts; 2) crusts; 3) nodules; 4) boundary between composition fields of basalts, nodules, and crusts of the Castor and Pollux guyots (a) and Magellan Mts. (b). Letters following sample numbers indicate: C) Castor; P) Pollux; M) Magellan Mts.

MINERALOGY AND CHEMICAL COMPOSITION OF Fe-Mn NODULES AND CRUSTS FROM SUBMARINE RISES

A highly localized method of transmission analytical electron microscopy (TAEM), x-ray diffractometry, and chemical analysis were used to investigate the mineral and chemical composition of Fe-Mn nodules and crusts. The TAEM experiment was carried out by means of a EM-100 electron microscope with a Keveks-5100 energy-dispersion attachment; this allowed us to obtain images, structural characteristics (based upon an analysis of the electron diffraction pattern), and information concerning element composition from Na to U all from a single mineral particle a fraction of a micrometer in size. X-ray phase analysis was carried out with the aid of a modified Debye-type camera alonging diffraction reflections to be recorded in the small-angle region. Analysis of the chemical composition of the nodules and crusts was performed by means of emission flame spectrophotometry and atomic-absorption spectroscopy on U4.2, AA-875 Varian pass-band modulator and Perkin-Elmer-403 instruments. Samples for examination were selected from successive zones of Fe-Mn-nodules and crusts, starting from their nuclei (bottoms) and ending with their external surfaces.

The Castor Guyot. This seamount has a height of 4.4 km (5500-1000 m). Its topmost portion is composed of organic limestones and volcanic breccia. A fragment of Fe-Mn-crust on limestone (Sample No. 20-2) was taken at depths of 2800-2500 m from a slope covered with fragments of basaltic rock (massive and amygdaloidal olivine basalt, plagioclase-porphry basalt, aphyric amygdaloidal basalt) and limestone.

The lower part of a crust (Sample No. 20/12) is composed of a black, pitchy aggregate of Fe-vernadite (Fig. 2a, b) and asbolane-buzerite (a small amount) (Fig. 3c, d). The outer zone of the crust is steel-black (Sample No. 20-12a) and pitch-black (Sample No. 20/12b); the color is due to Fe-vernadite and an Fe-x-mineral (see Fig. 3a, b). The brownish-black material of the minutely bumpy surface of a crust (Sample No. 20-12c) consists of Fe-vernadite.

Chemical analysis of different zones of crust (Table 3) indicate that the content of iron decreases from the surface of the crust to its lower portion and that the contents of alkali, magnesium, and nickel increase in the same direction. There are less distinct increases in the concentrations of calcium and chromium.

The Pollux Guyot. The guyot is ≈ 3.6 km (5000-1400 m) high and is crowned with a layer of organic limestone, whereas olivine and aphyric basalts enter into the composition of the lower portion of its flanks (4660-4120 m). Nodules

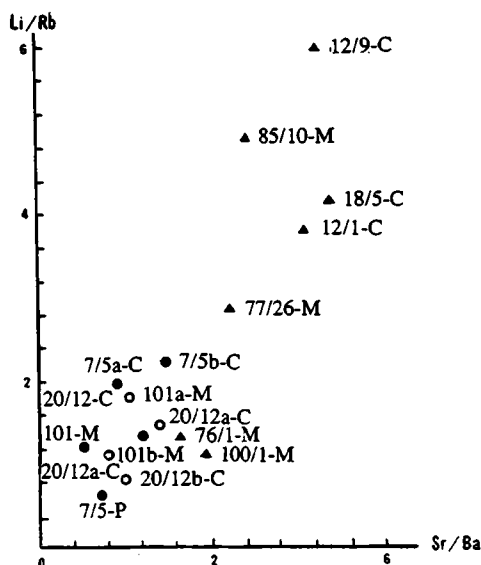


Fig. 5. Composition of basalts, Fe–Mn nodules and crusts in coordinates of Li/Rb–Sr/Ba. See Fig. 2 for explanation of symbols.

taken from depths of 1600-1400 m (Sample No. 7/5) are 5×9 cm in size; their surfaces are bumpy-rough and brownish-black in color. The inner part of a nodule is composed of black material (Sample No. 7/5) around a phosphorite core; iron-poor vernadite, goethite (lesser quantity) and asbolane–buzerite (very small amounts) can be identified within the core. The outer zone of a nodule 2-3 mm from the surface (Sample No. 7/5a) is composed of iron-poor vernadite ($\text{Fe}/\text{Mn} = 0.1\text{--}0.15$); Fe-vernadite ($\text{Fe}/\text{Mn} 0.4\text{--}0.8$), Fe–*x*-phase and birnessite are less abundant and Mn-feroxyhyte is also present in small quantities (see Fig. 2c, d). The material composing the bumpy surface of a nodule (Sample No. 7/5b) is primarily Fe-vernadite with a subordinate amount of goethite; individual flakes of asbolane–buzerite are also present.

The change in the chemistry of the material of the nodule from its surface to its core (see Table 3) is expressed by decreases in contents of iron and aluminum and increases in contents of calcium, sodium, potassium, barium, strontium, magnesium, nickel, chromium, copper, and lead.

The Magellan Mountains. From the slope of the seamount, where fragments of olivine vitrobasalt are found at depths of 2800-2000 m, we brought up a disk-shaped nodule (Sample No. 101) with a chocolate-brown mass in its center (Sample No. 101). This mass is composed of Fe-vernadite, a Fe–*x*-mineral, asbolane–buzerite, todorokite with $a_0 = 9.75$ Å (very small amount), and substantial quantities of apatite. The middle portion of the nodule is composed of Fe-vernadite, Mn-feroxyhyte, and a small quantity of goethite. The bumpy surface of the nodule primarily consists of Fe-vernadite, Mn-feroxyhyte, and small quantities of asbolane–buzerite as well as goethite (Sample No. 101b).

Variations in chemistry along a cross-section of the nodule (see Table 3) include a decrease in the content of iron toward the center of the nodule and increases in the concentrations of manganese, sodium, potassium, barium, strontium, nickel, and chromium.

Analysis of the data concerning the mineralogy and chemistry of the Fe–Mn nodules and crusts examined allows us to draw a number of conclusions concerning the origin of these rocks and their roles as concentrators of several indicator elements for sources of ore material.

According to well accepted diagnostic criteria [15], all the investigated nodules and crusts from the Castor and Pollux guyots as well as the Magellan Mts. are typical sedimentary (hydrogene) formations. The asbolane–buzerite, birnessite (buzerite 1), and possibly todorokite are results of a diagenetic process proceeding locally within nodules. These minerals are for the most part confined to the inner parts of nodules and the lower parts of crusts.

There is an interesting pattern in a nodule from the Pollux Guyot (Sample No. 7/5). The principal phase of the material in the upper part of the nodule is Fe-vernadite, but the inner parts of the nodule contain low-iron vernadite; this has been confirmed by chemical analysis. In addition, the presence of Mn-feroxyhyte has been established. The observed relationships between the above-mentioned minerals can probably be explained by bacterially driven recrystallization of the

Fe-vernadite originally formed (which is still preserved in outer, younger shell of the nodule) into low-iron vernadite and Mn-feroxyhyte or by formation of low-iron vernadite under conditions of an iron deficit.

Examination of correlations between the mineral compositions of nodules (crusts) and their chemical features reveals that cobalt is almost always present in the Fe-vernadite of the investigated samples and that asbolane-buzerite is the main concentrator of nickel.

There is a consistent increase in content of nickel and, in the majority of cases, chromium and magnesium toward the insides of nodules and the lower parts of crusts. This may indicate supply of these elements from basalts of volcanic submarine mountains.

EVIDENCE OF A CONNECTION OF Fe-Mn NODULES AND CRUSTS WITH THE COMPOSITION OF THE BASALTIC SUBSTRATE

As mentioned above, the elevated contents of Mg, Ni, and Cr which we and others have noted toward the bottoms of Fe-Mn crusts and cores of nodules may have resulted from efflux of these and other constituents from the basaltic substrate, especially in those cases where crusts grow directly on vents or fragments of basalt. Nodules contain fragments of these rocks in their cores. Since a similar distribution of Mg, Ni, and Cr occurs in the absence of direct contact between Fe-Mn formations and basalts, however, argument is not entirely convincing and a number of investigators dispute the existence of such a linkage [3].

It is reasonable to suppose that the discovery of similar chemical characteristics of spatially correlated between Fe-Mn formations and basalts would be evidence in favor of a definite connection between the compositions of the nodules, crusts, and basalts in specific areas of ocean crust. The absence of similar characteristics would be an objective indication that the compositions of Fe-Mn formations have no relationship to the compositions of the basalts in the region.

When comparing the chemical compositions of such different natural objects and basaltic rocks and Fe-Mn nodules or crusts, it is convenient to make use of elements common to all the objects in question and present in concentrations which can be compared; elements should also maintain their proportions during efflux from basalts and fixation in the material of the nodules and crusts. In accordance with this approach based upon chemical analyses of basaltic rock, Fe-Mn nodules, and crusts (see Tables 2 and 3) normalized to water-free and then element compositions, we computed Na/K, Ca/Mg, Li/Rb, and Sr/Ba ratios. The values obtained and their interrelationships are presented in graphic form.

On the Na/K-Ca/Mg plot (Fig. 4), it is evident that basaltic rocks in Fe-Mn formations found on the Castor and Pollux guyots, on the one hand, and found on the Magellan Mts., on the other, form separate, non-overlapping fields. This indicates that the rocks and nodules (crusts) of each region have similar chemical characteristics which, at the same time, distinguish them from rocks and Fe-Mn formations of the other region. Thus, rocks and Fe-Mn formations of the Castor and Pollux guyots generally show higher Na/K and lower Ca/Mg values than rocks and nodules of the Magellan Mts. These characteristics reflect the highly melanocratic nature and basicity of the basaltic rock association of the Castor and Pollux guyots, where picrites, picrobasalts, and olivine basalts with substantial contents of magnesium and lower contents of potassium are widely represented.

If basaltic rocks and Fe-Mn formations of one region were to show the same types of chemical differences from basites and Fe-Mn nodules (crusts) of another region, one could hypothesize the existence of a definite connection between the compositions of igneous rocks and Fe-Mn nodules (crusts) in each of these region. Such a connection would most likely reflect the participation of components supplied from the basaltic substrate in the formation of Fe-Mn nodules and crusts.

A Li/Rb-Sr/Ba plot (Fig. 5), on which these ratios show a positive correlation for both basites and Fe-Mn formations, suggests similar variability of geochemical parameters for basaltic rocks of seamounts and Fe-Mn nodules and crusts occurring on them.

There is a monotypic relationship between the compositions of such ore elements as Ni and Cu in basalts, Fe-Mn nodules (crusts), and the regional locations of these rocks. A plot (Fig. 6a) clearly shows that basaltic rocks of the Castor Guyot differ from basite of the Magellan Mts. in that they contain large amounts of nickel; both types of rocks show a trend of unidirectional change in Ni and Cu content. Contents of these elements in Fe-Mn nodules and crusts of both investigated regions vary in similar fashion (see Fig. 6b); this can be explained by assuming that elevated quantities of nickel and, probably, copper leached from the more melanocratic and magnesium-rich (in comparison with the Magellan Mts.) associations of basaltic rocks on these guyots participate in the formation of Fe-Mn nodules and crusts of the Castor and Pollux guyots.

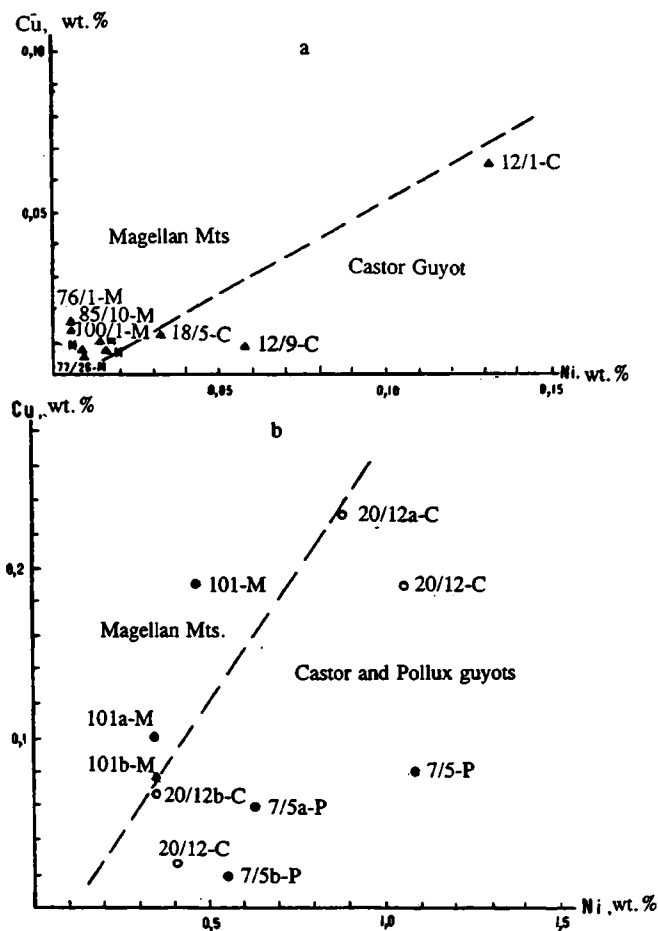


Fig. 6. Compositions of basalts of seamounts in Cu–Ni coordinates (a) and compositions of Fe–Mn nodules and crusts in Cu–Ni coordinates (b). See Fig. 2 for explanation of symbols.

On the basis of a comparative analysis of data concerning material composition of basaltic rocks, Fe–Mn nodules, and crusts from submarine volcanic mountains in the northwestern part of the Pacific Ocean, an analysis which reveals certain chemical characteristics common to both basites and Fe–Mn formations spatially associated with them, we can thus hypothesize a genetic connection between Fe–Mn nodules (crusts) and local basaltic substrate. This connection is a result of the fact that the formation of nodules and crusts involved the participation of a number of elements which were leached from basalts during their halmyrolysis into near-bottom waters and sediments and which were subsequently captured by defective layered (asbolane – buzerite) or pseudolayered (Fe-vernadite, Mn-feroxyhyte) minerals of hydrogenic crusts and nodules during their formation and transformation.

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JURASSIC EVOLUTION OF THE TIEN-SHAN

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UDC 235.2:551.8(551.762)

Complex studies led to identification of three stages in Jurassic deposits. The stages reflect development periods of the studied deposits. Each stage is represented by a paleogeographic map that indicates the evolution of ancient landforms in the Tien-Shan region in time and space.

For two reasons the Jurassic Period was important to geologists.

Jurassic paleogeographic processes may be related to the development of major transgressions and regressions. In addition, various Tien-Shan mineral resources, primarily oil, gas, coal, bauxite, mineral placers, and others developed generally in continental blocks.

Major changes were associated with the Jurassic paleogeographic, paleotectonic and paleoclimatic conditions. In this respect, the Tien-Shan Block offers a unique depositional model for similar continental basins in the Ural-Mongolian region. My study deals with Mesozoic Tien-Shan Basins (Fergana, East Fergana, Kavak-Issyk-kul', Fan'-Yagnobsk, Nazar-Ailoksk, etc.). Jurassic deposits occupy basins (e.g., Fergana) in the marginal zone. In others (Fan'-Yagnobsk, Nazar-Ailoksk, etc.), they act as tectonic wedges between Paleozoic rocks.

This paper reports results of detailed studies of lithofacies characteristics and paleogeographic reconstructions in evaluating mineral resource prospects.

The Jurassic section that fills Mesozoic basins includes many facies. Continental alluvial, lacustrine, swampy-lacustrine and swamp deposits alternate.* Previously, the author undertook a complex study, involving lithofacies, mineralogy and petrology, employing most recent biostratigraphic data. Three stages correspond to specific stratigraphic horizons and include one phase of the region's geotectonic development [4, 17]. Each stage reflects depositional condition changes between individual stages [4], as well as composition of plant communities [1, 2, 6], climate [10], sediment composition [5, 15] and other aspects. The sediment complex of each stage is subdivided on the basis of region unconformities.

Jurassic deposits formed in three major stages associated with the Lower Jurassic-Aalenian, the Bajocian-Bathonian, and the incomplete Callovian intervals.

A brief description of the pre-Jurassic surface relief precedes paleogeographic reconstructions of the region.

Pre-Jurassic (Late Triassic) Stage (Fig. 1). The beginning of the Late Triassic stage was characterized by lack of intense tectonism and widespread early Mesozoic peneplain development on all continents. Currently the existence of an early Mesozoic peneplain, global in dimension, is under discussion. A series of coalescing peneplains may have existed. However, major mountain areas, as the Ural, Tien-Shan, Salair, Altai, and all structures of the Laurasian continent had been reduced in elevation in early Mesozoic times. Early Triassic rifting along the periphery of the Siberian and East European Platforms coincided with peneplanation.

Several workers [3] explained rifting by dextral rotation of the West Siberian Platform at the end of Permian and the early Triassic. In certain areas compressive forces were dominant, leading to block mountain formation. Other areas experienced dilatation and subsequent rifting.

Many geologists consider large parts of Central Asia and the Turan Platform, similarly to West Siberia, peneplains where maximum early Mesozoic leveling had taken place. Small piedmont-terrains and a poorly integrated hydrographic network developed (Fig. 1).

*The author did not study swamp deposits.

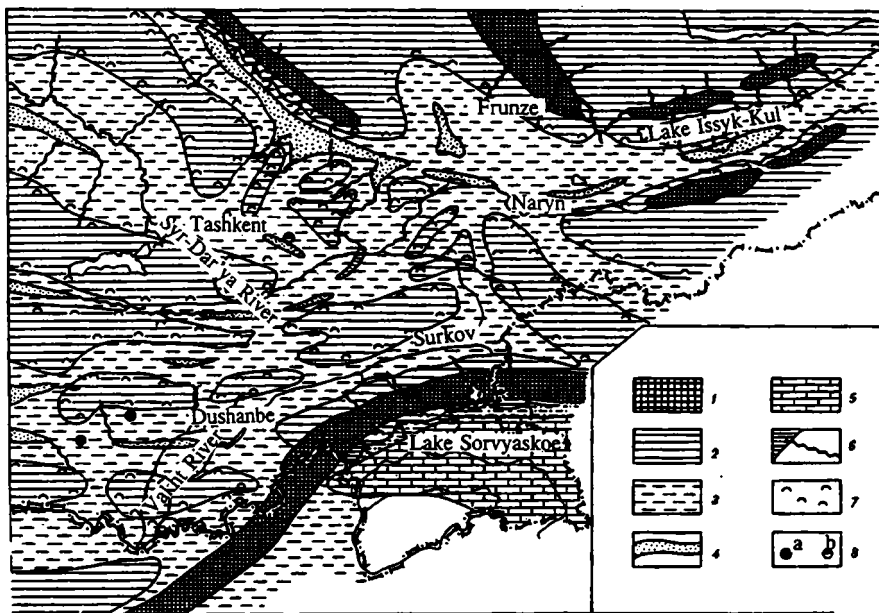


Fig. 1. Paleogeography of Tien-Shan in pre-Jurassic – Late Triassic times: 1) Lower Jurassic block mountains; 2, 3) dissected peneplain (2 – high; 3 – low); 4) lacustrine – alluvial valleys; 5) marine limestones; 6) lake-type small rivers; 7) weathering horizons; 8) complete weathering horizons.

In contrast with sharply defined early-mid Triassic arid stages, the Late Triassic of Central Asia and Kazakhstan was characterized by wetter climate and widespread distribution of chemically weathered soil horizons. South Kazakhstan and Tien-Shan land areas were raised in the late Triassic [10]. Lateritic weathering horizons formed here. Due to erosional incision of the land surface, sediment accumulation was restricted.

The 1983 paleogeographic map of the USSR indicates broad areas of nondissected peneplains, rimmed by dissected ones. Medium-sized mountains and foothills occur in the Dhalair – Neimansk Range and the present Gissarsk and Turkestan ridges. Relatively small, locally slightly swampy river valleys occur in them. The weathering horizons, preserved during the current denudation phase only in basins, earlier were more widespread, both in dissected and the nondissected peneplains. The dissected plains were associated with thicker and more intensively reworked, often bauxitic weathering profiles. In nondissected peneplains, relatively thin weathering horizons, essentially clayey montmorillonitic or kaolinitic – illitic profiles, occur in massif-rims, subjected to peneplain development. Almost all the largest and most productive bauxite, kaolinite, gold, and rare-earth-bearing weathering horizons were associated with dissected peneplains.

Lower Mesozoic-Upper Triassic bauxitic weathering horizons are known from Fergana, Kavak, Issyk-Kul', Fan' – Yagnobsk, and other basins where they were preserved only under Mesozoic and Cenozoic covers. They occur along the rims of younger, early Jurassic coal-bearing grabens. This pattern is typical of ural and Siberian platform-margin zones. Weathering horizons were preserved in the southernmost basins of the Afghan – Tadzhik Depression where they developed mostly in basic margins. They occur in large areas in large areas of the western Hindukush, northern Pamir and the Parapariz [9].

An extended period of leveling of the Hercynian mountain structures preceded pre-Jurassic times. Paleogeographic maps indicate the resulting landforms (Fig. 1).

Lower Jurassic – Aalenian Stage. The start of the Jurassic sedimentary cycle was marked by a sharp increase in tectonic activity in the Asian continent and adjacent areas. A complex, dissected relief developed, with many mountain structures, basins, valleys. Two main relief categories developed. The first includes the Syr-Dar'ya, Chatkal – Kuraminsk, Chu – Iliisk, Naryn and Tarim Uplifts. These are large crustal tectonic blocks, represented by undulating denudational surfaces with individual, reduced arches and huge ancient, strongly dissected mountain ranges (Fig. 2).

The second type corresponds to heavily dissected high mountain ranges. The largest ones, the Turkestan, north Alaisk, Gissarsk and south Alaisk are divided by the Sokh water divide between the East Fergana and Fergana Basins. Their absolute elevation exceeded 800 m in Late Jurassic times [8, 10]. They also formed a natural paleobasin boundary and a bar-

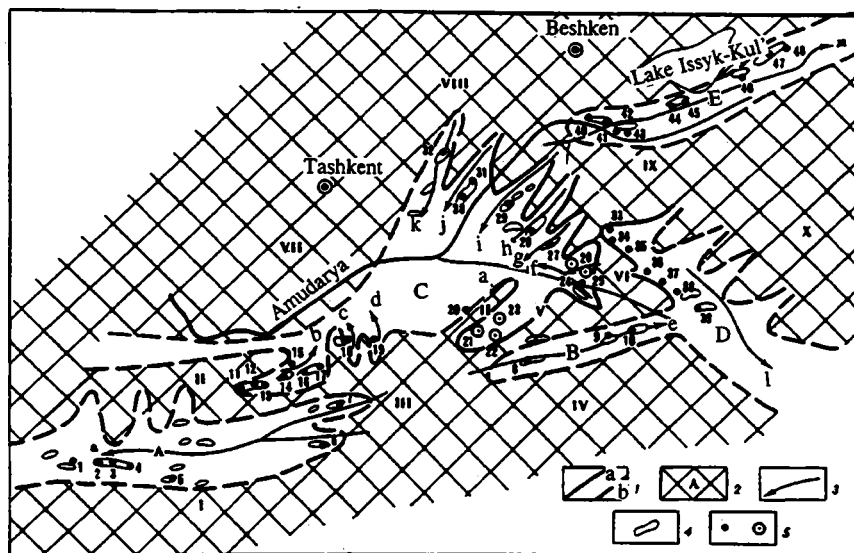


Fig. 2. Paleogeomorphologic structure map of the Jurassic surface: 1) contour of paleo-highs (a – assumed; b – established); 2) paleo-high (I – Gissarsk; II – Turkestan; IIa – Karachatyry Ridge; III – Sokh water divide; IV – Gissarsk–Alaisk; V – Turkestan–Alaisk; VI – Yssinsk water divide; VII – Chatkal'sk; VIII – Kuraminsk; IX – Naryn; X – Tarim. A-D) ancient basins (A – Zeravshan; B – Kichikalaik; C – Fergana; D – East Fergana; E – Kavak–Issyk-Kul'); 3) ancient stream systems; a) Zeravshan; b) Sulyukta; c) Guzan; d) Rishan; e) Kichikalai; f) Irisu (Aldyyar); g) Karangur; h) Kok–Yangak; i) Mailisu; j) Shurab; k) Arkit; l) Alaiku; 4) outline of present Jurassic outcrops; 5) studied outcrops (a); drillholes (b): 1) Tavasang; 2) Dzhidzhikrut; 3) Ravat; 4) Pasrud; 5) Ziddy; 6) Nazar–Ailoksk; 7) Sokhl; 8) upper course of Kichikalai River; 9) right bank, Kichikalai River; 10) Khodzhekelyan; 11) Kokkiya; 12, 13) Sulyukota; 14) Garm; 15) Mayadygen; 16) Shurab; 17) Samarkandek; 18) Guzan; 19) Rishan; 20) Kavak; 24) Aldyyar (Irisa); 21-23; 25, 26) drillholes of Kirgizistan Geological Survey; 27) Kunduk; 28) Kok–Yangak; 29) Mailisu; 30) Tashkumyr; 31) Tegenek; 32) Arkit; 33) Kokkiya; 34) Tuyuk; 35) Karatepe; 36) Chitty; 37) Kurutash; 38) Uchat; 39) Alaiku; 40) Kavak; 41) Kavak-1; 42) Karakichie; 43) Bazaigur; 44) Azhabibulak; 45) Suguty; 46) Dzhergelan; 47) Dzhergelan-1; 48) Tyup.

rier that kept the Jurassic marine basin from intruding into the Tien-Shan depositional basin.

Basins, located between the old uplifts were gradual buried during Mesozoic and Cenozoic times. The Fergana Basin is the largest of these. It formed between the ancient Chatkal–Kuraminsk Uplift on the north-northwest, the paleo-Turkestan Basin on the south, and the ancient Yassinsk water divide on the east.

Assumptions about a merger between the paleo-Fergana and the East Fergana Basin [14] are unproven [5]. These paleobasins formed independently of each other. This is shown by deposition of the Upper Jurassic Koshbulak Formation over the Paleozoic basement in the Yassinsk Uplift. The uplift was the water divide between the two basins throughout the early Jurassic and in part during the late Jurassic. Consequently, the Fergana Basin was isolated on the east by the ancient Yassinsk divide, although this isolation was not complete. If it were, flooding Jurassic streams would have filled the Fergana Basin during the short time interval. Water from the Fergana Basin then would have spilled over between the ancient uplifts into a series of depositional basins, such as the paleo-Zeravshan, East Fergana Basins and others. However, this scenario is unproven by our data. Detailed lithofacies analyses of the outcrops indicated [5] that the Fergana Basin most likely was open to the west. Water erosion cut through a narrow valley, located between two ancient highs, the Chatkal–Kuraminsk and Turkestan Uplifts. The valley formed along an ancient deep fault, oriented in the E–W direction. Alpine tectogenesis probably pushed these two uplifts toward each other along the fault. As the result, Jurassic sediments were either eliminated or buried under older deposits. Portions of the present Syr-Dar'ya Basin probably incorporate Jurassic basins that are buried under younger sediments. In the future, these formations may become practically important to geologists.

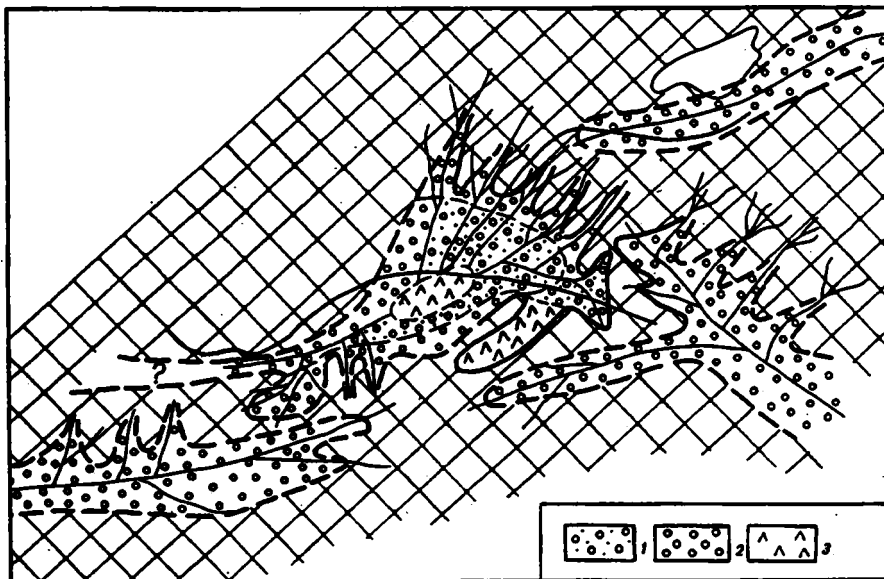


Fig. 3. Paleogeographic map of lower half of Lower Jurassic–Aalenian Stage. 1-3-paleo-landscapes (1 – mountain river; 2 – mountain-lowland plain or lowland plain-mountain stream; 3 – lacustrine).

An east–west oriented river valley exist on the east. Its individual remnants presently occur in the Kavak, Karakichie and Minkish areas and along the south shore of present Lake Issyk-Kul'. Two separate Jurassic valleys have been identified here [14]. The first was thought to occur in the Kavak region and entered the East Fergana Basin. The second, followed the present shore of Lake Issyk-Kul' and extended eastward. The valley was not more than 10-20 km wide. Toward the east, in China, it combined with other Jurassic basins. The presence of a single river valley is indicated by the identical lithofacies and compositional makeup of the sections in different parts of the basin, and by their cyclic characteristics. These prove the synchronicity of geological events and the identical composition of terrigenous mineral associations.

Based on characteristics of the accumulating sediments, at the time deposits of the first stage started to form the entire region has been strongly dissected. Dissected relief is also indicated by the phytogeographic zonation of the Lower Jurassic flora. A mixed cycad-*Ginkgo* phytocoenosis occupied the ancient river valleys. Its distribution pattern was uneven, as if outlining a meandering valley. An essentially *Ginkgo*-bearing assemblage characterizes the ancient uplifts (paleo-Gissar–Alai, paleo-Turkestan–Alai Uplifts, etc. [10, 11, 14, 15]). Thus, the paleomorphostructural elements (eroded uplifts, intermontane basins and depressions) formed during the first stage. This fact predetermined the depositional processes on the Eurasian crustal plate not only in the Jurassic but also in later epochs. Subsequent landform evolution inherited these older structural elements.

The Zeravshan Ridge and the axial part of the Alaisk Ridge, presently of 4000-5000 m elevation, occupy locations, occupied in the part by the Zeravshan and Kichikalisk intermontane basins. Only relicts of these structures exist in the form of tectonic blocks. The largest include the Fan'–Yagnobsk, Nazar–Ailoksk and Khodzhekelyansk structures.

Two large elongated, narrow graben-like basins, the Karatau and East Fergana Basins, occur along the Talas–Fergana Fault. The East Fergana Basin southeastward is transitional toward the Yarkend Basin.

A paleogeographic summary of each depositional basin follows.

The First of the Lower Jurassic–Aalenian Stage saw establishment of the Fergana Basin and its basic morpho-structural elements. At this time, the relief was severely dissected. This relief was related to numerous pre-Jurassic uplifts and basement ridges. The basic rim was incised by a number of river systems (Fig. 3).

The southern and southeast basin margins included a number of river valleys. The largest were the Greater Sulyukta and the Greater Irisu (Aldyyar). The upper reaches of the Greater Sulyukta River had an east–west orientation that changed abruptly in the Shurab region to a north–south course. The rivers were typical mountain streams, confirmed by the coarse river channel deposits and lenticular beds, embedded in the talus-slopewash deposits. Numerous intraformational unconformities in the channel deposits were related to very unstable depositional conditions that prevailed in the stream valleys.

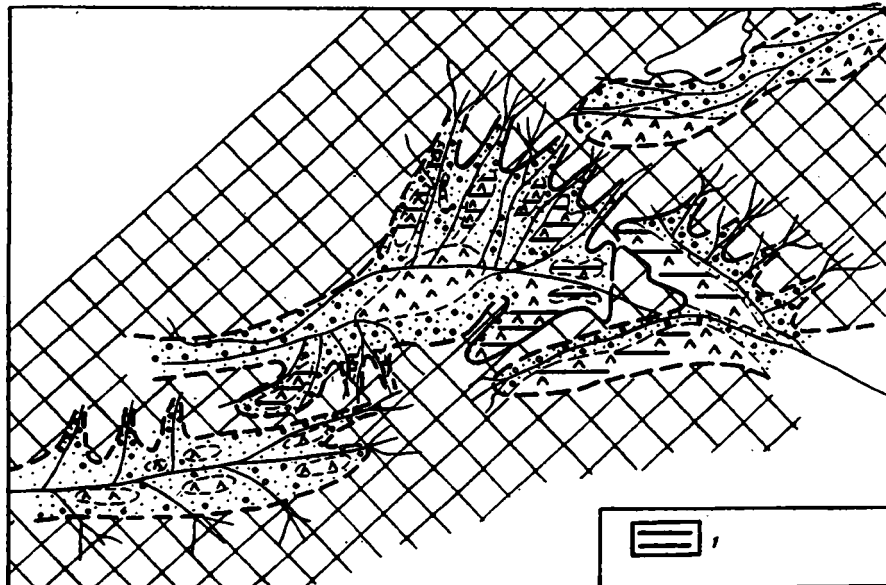


Fig. 4. Paleogeographic map of upper half of Lower Jurassic – Aalenian Stage.
1 – lacustrine swamp and swamp paleo-landscape. Other symbols: Figure 3.

Depositional conditions are somewhat different in the Kizil–Kiya area. Relatively large lake bodies occurred between the paleo-Karatyr, on the north, and paleo-Turkestan, in the south. The absence of coarse matter in the sediments indicates deeply incised relief, framed by ancient uplifts.

In the eastern, northeastern and northern rim zones depositional conditions resembled those of southern Fergana where alluvial landforms were predominant. These developed by fluvial processes in the Greater Arkit, Greater Tashkumyr, Greater Milisu, and other streams. Upstream, all rivers were narrow, with steep, dissected banks. The systems widened toward the basin center, and forming a gravelly–sandy alluvial plain, coalesced.

All these stream valleys that formed in the early Jurassic deposition stage along the Fergana Basin rim, have been reshaped by the changes in the thickness and composition of the sediment fill. Until recently, depositional conditions of the sediments in the central basin area were still unknown. Sediments here are buried under a 12-km Mesozoic–Cenozoic sequence. As Yu. V. Stankevich and M. I. Simonenko also stated, a large lake occupied the Fergana Basin in the Lower Jurassic. Intensive reactivation of the Talas–Fergana Fault resulted in the formation of the East Fergana depositional basin in this fault zone. The basin represented one of the largest and most intensive downwarps, as shown by the accumulation of 800-m coarse detrital deposits within a short time interval. Poor sorting, the presence of conglomerates and boulders, and the identical composition of eroding source rocks, all point to a small distance that separated the sedimentary basin from its source areas.

The present Zeravshan and Alaisk Ranges occupy areas of the paleo-Zeravshan, respectively, paleo-Kichikalaish Basins. These E–W oriented landforms coincide with deep basement fault trends. As later confirmed [5, 17], there was a strong genetic relationship between deep basement structures and river valley orientation.

The Kichikalaish Basin opens eastward toward the Yarkend–Fergana Depression. This is indicated by coarse, alluvial, detrital deposits, displaced by alluvial, lacustrine-swamp facies by gradual westward tapering off of the lower horizons. The Cretaceous–Paleogene deposits overlie the Paleozoic basement along the upper course of the Kichikalai River.

The paleo-Zeravshan Basin, probably opened toward the northwest. This is shown by increased ratios of coarse-grained sediments. During the early stages of the Jurassic cycle, sediment accumulation took place in narrow grabens during highly variable depositional conditions. Numerous mountain river systems shed coarse detrital sediments from the ancient Turkestan–north Alaish and Gissarsk–south Alaish uplift areas.

The Caucasus–Issyk-Kul' river valleys developed northeast of the E–W oriented Yarkend–Fergana Basin. The Basin's southern boundary coincides with the present outcrop outline of Jurassic beds. The northern basin boundary probably crossed the northern part of present Issyk-Kul' Lake. This is indicated by Neogene–Quaternary deposits that overlie the Paleozoic basement beneath the northern lakeshore.

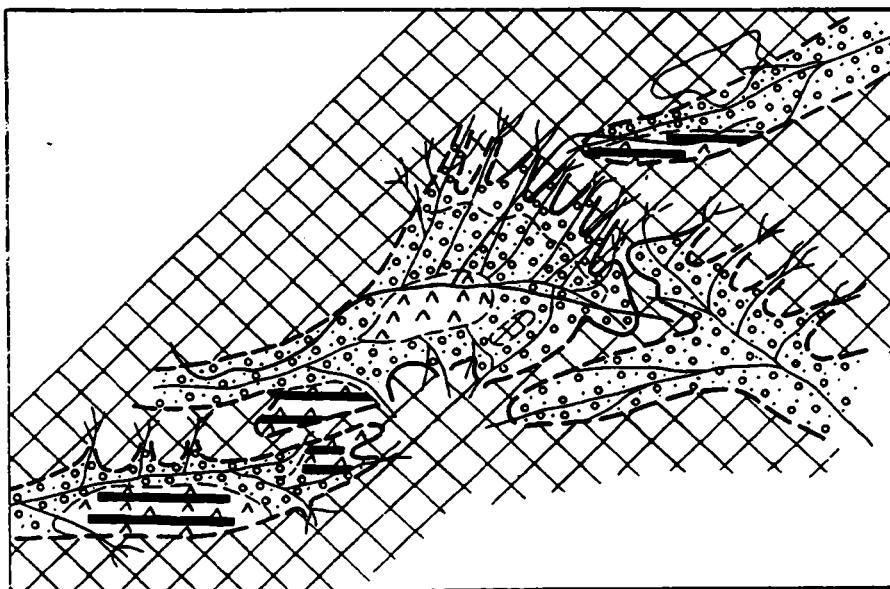


Fig. 5. Paleogeographic of lower half of Bajocian–Bathonian Stage. Symbols: Figure 3.

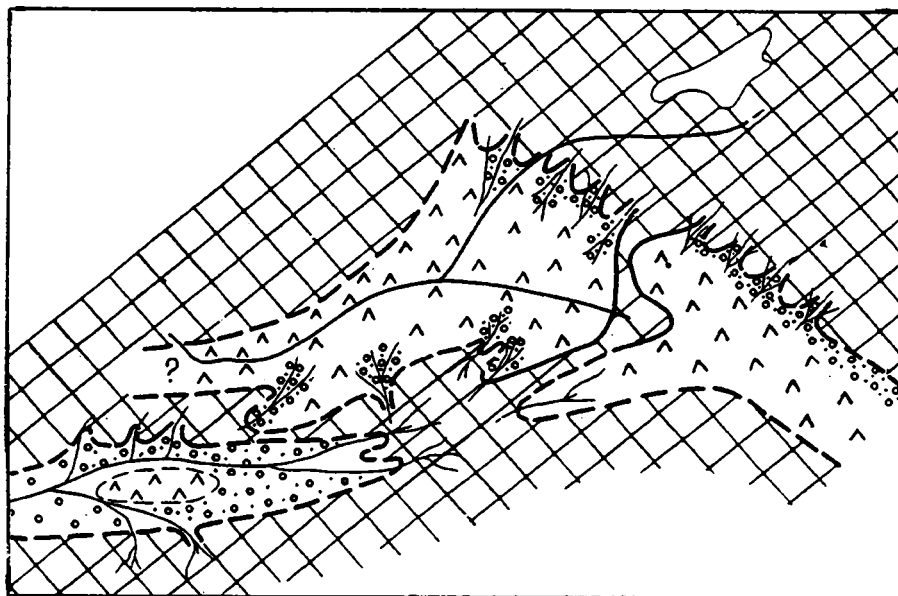


Fig. 6. Paleogeographic map of upper half of Bajocian–Bathonian Stage. Symbols: Figure 3.

The main fluvial sequence formed in the central valley area. Many streams supplied terrigenous deposits to the trunk river. Textural and structural characteristics of the Jurassic deposits, in combination with overall depositional lithofacies zonation indicates the eastward transport of terrigenous sediments. Alluvial conditions generally prevailed in the valley. The low concentration of coarse detrital rocks and their frequent absence points to the weak dissection of the surrounding ancient uplands. Lake and lacustrine-swamp conditions were associated with the inherited pre-Jurassic plain, adjacent to the main uplift areas and ridges. Extensive conversion of lakes into swamps resulted in peat bog formation in the Kavak and Dzhergelan areas. The resulting coal beds are 2-15 m thick.

During the **second half of the Lower Jurassic–Aalenian** major changes impacted depositional conditions. Lacustrine, swamp and lake landforms started to form. These depositional facies occurred in river valleys, associated with coal beds and prospective coal deposits. The lenticular nature of coal beds and enclosing unit indicate a highly dissected surface relief. Coal beds in correlation with peat bogs, were thickest in the central swamp areas. Along swamp margin the coal beds became subdivided into thinner units and their composition became more complex. They include sandstones,

gritstones, often even conglomerate beds. Similar coal beds, even thicker ones may be buried in stream valleys located along the south basin flank, between Guzan and Pishan.

Intensive thick peat bed accumulated in the Naukatsk Basin. Conversion into swamplands and siltation of previous lake bottom led to formation of peat deposits, the thickness of which reached and exceeded 100 m. Presently the coal beds are 10 m thick.

Landforms of the east, northeast and the east rim of the Fergana Basin include north-south oriented (Greater Ankit, Greater Tashkumyr) and east-west-trending (greater Karangur, Greater Mailisu, Greater Kok-Yangak) river valleys. In contrast with earlier conditions of predominant alluvial deposition, lacustrine and lacustrine-swamp facies evolved. These facies gradually disappeared in the basic center, but became more prevalent along flanks of the ancient uplifts.

Substantial changes occurred in the second half of the first stage in the Yarkend-Fergana Basin (Fig. 4). Alluvial conditions ceased to exist. A large lake occupied the area and in the final stage intensive swamp development took place. Large peat bogs formed, the largest between the Kumbel' and Karashur sectors. The peat bogs abruptly tapered off toward the southeast and disappeared altogether at Alaika village. This apparently was due to the merger of three fluvial systems of Alaika. Two streams originated in the Tarim land area, the third in Kichikali Basin. Supplying large water volumes to the lakes, they prevented peat bog development.

Fluvial and lacustrine swamp landscapes developed in equal proportion in the Kavak-Issyk-Kul' Basin. Peat bogs were restricted to small local areas. They were associated with small lake bodies. However, despite their small dimension, peat accumulation was so intensive in these bodies that 100-m peat beds developed in a relatively short time. Presently, coal beds are maximum 15 m thick at Kavak and Kakichie. Toward the east, peat beds in the swamps were only 20-30 m thick.

The paleo-Zeravshan Basin had been converted into an incised intermontane valley with lacustrine-swamp facies. A conifer-*Ginkgo* assemblage grew on uplands and flat slopes [10, 11]. The luxuriant vegetation that included *Polypodiaceae* ferns, fern palms, and *Bennettitales* favored peat development. These processes were most intensive in the Ravat, Sokh and Nazar-Ailoksk. Presently, coal beds, 5-10+ m thick and of complex composition occur here. As earlier, alluvial conditions dominated the ancient uplifts.

Landforms in the Kichikalaisk Basin were inherited from previous periods. However, along with alluvial conditions, lake, and lake-swamp facies also occurred. Thick peat beds formed, as at Khodzhekelyansk.

In conducting the brief account of landscape evolution, during the Zeravshan period the first development stage was characterized mostly by denudational leveling of the land surface. A sharp increase took place in lake and lacustrine-swamp sedimentation. This period had seen the maximum development of the peat bogs that led formation of presently known and prospective coal deposits. A varied and luxuriant vegetation provided the preconditions for this in the basic.

Plant community studies [7, 12, 13, 16, etc.] indicated a very close relationship between Jurassic landscapes and phytogeographic zones. Four phytzones occurred: (1) an essentially cycade association, with diapters, matoni and rare *Ginkgos*; (2) a mixed *Cycadaceae*-*Ginkgo* association, differing primarily in the even amounts of *Ginkgos* and *Cycadaceae*; (3) an essentially *Ginkgo* assemblage, and (4) a pure *Equisetum* (horsetail) assemblage.

The floral distribution leads important paleogeographic conclusions. *Cycadaceae* and ferns dominated in the south, along the Mesotethys shores. A mixed complex lived in river valleys in the paleo-Gissar, Fergana and East Fergana areas. Their uneven, meandering outline delineated ancient river courses. The third phytocoenosis occurred on the Lower Jurassic uplifts of the paleo-Turkestan and the Tien-Shan interior basins (Kavak-Issyk-Kul' Basins).

Bajocian-Bathonian Stage (Figs. 5-6) A sharp increase in tectonism resulted abrupt changed sediment accumulation patterns in the Tien-Shan intermontane basins. The earlier widespread lacustrine and lake-swamp facies, characteristic of the early second stage, except in the southern Fergana Basin disappeared completely. The left-hand tributary of the Greater Sulyukta (Samar-Kadek) and the Kargash (Yarkend-Fergana Basins) was still associated with stable lacustrine-swampy, and lacustrine conditions. Alluvial facies emerged and prevailed in the rest of the Fergana Basin. The Yarkend-Fergana Basins received the most intensive influx; 800 m of sediments accumulated in a brief time interval. As indicated by the large number of intraformational erosional unconformities within the Jurassic section, the sedimentary processes have undergone abrupt changes in time and space.

The paleogeography of the Zeravshan Basin resembled that of the first stage at the start of the second. Lacustrine and lake-swamp conditions dominated. Varied peat beds of different composition occurred in the Fan'-Yagnobsk region. More than 14 coal beds of varying thickness formed subsequently. The most promising commercial coal beds are 5-9 m thick in the middle part of the section. Intraformational erosion reduced their thickness at Ravat and Nazar-Ailoksk.

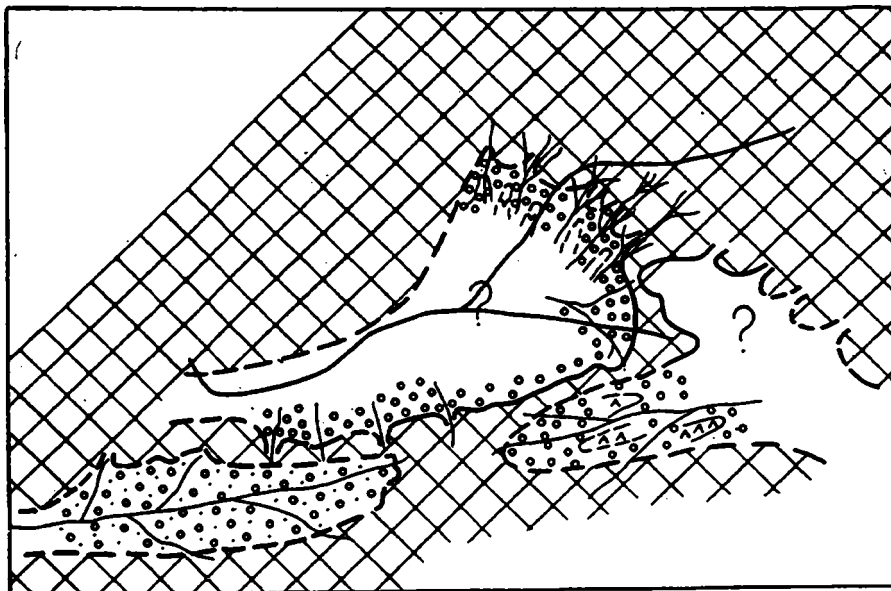


Fig. 7. Paleogeographic map of the Callovian Stage. Symbols: Figure 3.

The uniform thickness of coal beds and the enclosing rocks indicate the large size of the lakes. Peat formed from the same plant matter as in the previous stage. However, the distribution area was significantly reduced by meandering streams that often interrupted the peat accumulation (Fig. 6).

The second half of the second stage coincided with maximum lake development not only in the internal continental Tien-Shan Basin basins, but also over a vast, young Epihercynian platform area.

Lake formation coincided with a major Mesozoic transgression. This unique event was associated with significant increase in precipitation, to 2,000 mm/yr [15, 10]. This influenced the entire ground water regime and led to the development of large fresh water lakes (Fig. 6).

Paleogeographic changes accompanying deposition in the second half of the second stage resulted in flora changes. Continued transgression of the Mesotethys, peneplain development on piedmont and unplanned areas followed. River valley evolution led to northward migration of warm-climate floras on the continent. T. N. Sikstel', A. M. Kuzichkina and others have described general aspects of phytogeographic zones of the preceding stage. However, the inherited, relatively col-climate forms became limited in the north and on local uplifts. Their distribution area was markedly reduced. The *Cycadiaceae* occupied areas south of the basin and the semicircle along the landward margins of the transgressive onlap zone. Sikstel' outlined a mixed *Cycadaceae*–*Ginkgo* phytogenetic zone in the Gissar–Fergana region.

Callovian Stage (Fig. 7). Three basic factors impacted landscape evolution during sediment accumulation of the third stage: an abrupt increase in tectonism in the depositional basins, the transgression of the Mesotethys, and the change from humid to arid climative conditions.

All basins were partially eroded during this time, accompanied by arid weathering processes. This is shown by the sporadic occurrence of sediments of the third stage along the mountain margins of the basin. The Kavah–Issyk-Kul' Basin was terminated and became eroded. Absence of third stage deposits in sections of the East Fergana Basin apparently is also connected with the basin's disappearance.

A series of alluvial fans and small lakes developed along rims of the Fergana Basin where rivers emerged from old uplift areas across the mountain margin. Colors of variegated terrestrial deposit complexes ranged between bright red, green and cinnamon-brown. Dolomite and anhydrite layers and the absence of plant matter indicated extreme aridity in the third stage, not only in the Tien-Shan but also across the entire Asian plate surface. Geophysical data indicate that the lower Mesozoic sequence became much thinner in the basin. This apparently marked the termination of sediment accumulation. Subsequently, all Jurassic basins were uplifted and eroded. These conditions were global and involved the largest, Ural–Mongolian continental block.

This stage south of the Mesotethys corresponds to the Oxfordian–Kimmerdgian Stage. The Yassinsk watershed continued to exist. However, it was subdivided into a number of small, flat basins that received variegated terrigenous

deposits of deltaic and talus (slopewash) origin. The deposits wedged out abruptly toward the basin margin and were absent in the water divided area.

The paleo-Zeravshan Basin was converted into an alleviated area, and the Kichikalaish Basin to a site of alluvial and lacustrine sedimentation.

* * *

A complex study of the Tien-Shan continental complexes led to their subdivision into three stages. Each stage represents essential changes that affected Jurassic deposits of the Tien-Shan block.

The first half of the Lower Jurassic–Lower Aalenian Stage experienced a sharp increase in tectonic activity. The earlier formed peneplain was destroyed and the basic morphostructural elements of the uplift, basin and fluvial system were established. Structural elements of the present Mid-Asian Block largely inherited these relief features that had developed during the first Lower Jurassic–Aalenian Stage.

Due to enclosed placer deposits (tourmaline, zircon, occasionally gold) the alluvial beds of the fluvial system of this period are of practical importance.

The second half of the Lower Jurassic–Aalenian Stage coincided with reduced tectonism. River valleys and basins widened. The rich vegetation cover, abundant moisture, incised landforms led to lake-swamp and swamp development. This period is associated with the greatest peat bog development. Their subsequent conversion resulted in commercial and prospective coal deposits. The prospective coal areas included a buried river systems along the south rim of the Fergana Basin. Renewed tectonic movement in the first half not the Aalenian–Bajocian interval destroyed the earlier formed landforms. Alluvial conditions dominated all basins. Large fresh water lakes became very widespread from the second half of the Aalenian–Bajocian interval. They occurred not only in Jurassic basins of the Tien-Shan block but also in the entire Ural–Mongolian region. Finally, due to renewed tectonism and shift to arid conditions, another depositional shift took place in Callovian times. Sedimentation became sporadic. All Jurassic basins became extinct at the end of the Callovian and have underwent erosion. This was the start of the Cretaceous sedimentary cycle.

Paleogeographic reconstruction, based on basic time intervals, thus generated general assumptions on the specific depositional conditions in each depositional basin. This allowed the understanding of their evolution in space and time and the identification of those landscape and paleogeographic zones that are most likely to be associated with the formation of sedimentary mineral resources.

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LITHOLOGICAL, GEOCHEMICAL AND PALEO GEOGRAPHIC PROBLEMS OF THE CENOZOIC DEPOSITS OF THE PRECAUCASUS REGION

PART 2. PALEOSTREAM IMPACT ON DEPOSITIONAL CONDITIONS IN PRECAUCASIAN BASINS

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UDC 550.4:552.5:551.77(479)

The paper deals with the role of major platform rivers during accumulation of the Maikop deposits in the central and eastern Precaucasus region. Paleostream data in Maikop, Lower Jurassic, Middle Miocene and Middle Pliocene times provided information on the activities of major platform streams that constructed deltas in the eastern and northeastern parts of the eastern Precaucasus. Bedload transport played a role in east Precaucasian sediment accumulation. It significantly impacted central, possibly also the western Precaucasian areas.

Analysis of mineralogical—geochemical conditions of two stratotype sections of the Maikop Series along the Sulak (eastern Precaucasus) and Kuban' Rivers (central Precaucasus) proved the existence of major platform streams throughout Maikop times. Fluvial sediments accumulated in the eastern and central Precaucasus [17].

The terrigenous sediment flux of the major rivers, ancestors of the present Volga and Don, superimposed a very well defined imprint on the east Precaucasus lithofacies pattern. Unfortunately, the Maikop deposits of this region are exposed on the land surface only in a narrow zone. Drillholes scarcely encountered Maikop beds in the eastern Precaucasus. However, data clearly indicate the presence of major Russian Platform streams during Maikop times. These entered the Maikop sea in the present north Caspian area and influenced sediment accumulation in the east and apparently also the central Precaucasus.

Data presented were primarily based on drilling information. At least 13 sandy—silty—clayey units occur in large areas of the eastern Precaucasus, including the south slopes of Karpinsk, Chernolesk Basins, the Prikumsk—Tyulenevsk Arch and adjacent areas [4]. Thick Maikop, mostly mid-Maikop deposits, occur in an area of over 40×10^3 km². These units include 3-12 sand beds that, from oldest gradually taper off in a westward direction. The sand content increases eastward and attains a maximum 36-44% in the Kizilyarsk Bay areas. Drill data on which this information is based, thus clearly show that large volumes of terrigenous deposits entered the northeast basin from the platform area. This sediment flux was due to transport and deposition of terrigenous deposits by major platform rivers in depocenters, including submarine fan prodeltas and deltas.

New means of lithofacies analysis and recent lithostratigraphic reconstructions by seismostratigraphic methods indicated the widespread distribution of sedimentary basins. Seismostratigraphic analysis of the sediment cover has been conducted in the eastern Precaucasian region [14]. Analysis of the Maikop beds revealed a sequence of clinoform structures, subdivided into eleven clinoform seismofacies. They are characterized by sandy—clayey composition, with a dominant clay component (Fig. 1). As earlier claimed, terrigenous matter had been supplied from easterly and northeasterly sources in the present north Caspian region. The clinoforms formed on submarine slopes and relatively deep marine areas under conditions of sediment imbalance. Overlapping lobate Maikop lithosomes reflect episodic supply of terrigenous matter from a northeastern source and increase in sediment volume with time.

Seismostratigraphic data of the Maikop beds agree with the drilling information. This and other findings confirm the presence of large volumes of terrigenous source sediments in the north Caspian region. The sediment volume is reflected by the dimensions of sediment bodies that formed as the result [4], approximately 5 to 40×10^3 km². The clinoform lithosomes are 90-300 km long, 40-50 km wide and several hundred meters thick. Their volume ranged between 1.2 - 2.2×10^3 km³

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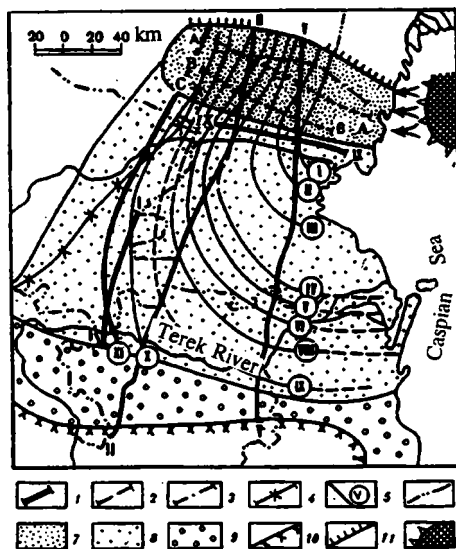


Fig. 1. Investigated areas and regional OGT profiles of the eastern Precaucasus [14]: 1-4) regional profiles (1 – PO Grozneft egeofizika; 2 – based on correlations; 3 – PO Volgogradneftegeofizika; 4 – PO Stavropol'neftegeofizika); 5) paleo-shelf edge, with Maikop bed clinoform seismofacies [I-IX-numbered units of Maikop clinoform series]; 6) administrative boundaries; 7) area of detailed seismostratigraphic profiles; 8) area of W and SW dips of Maikop clinoforms on regional and other seismic profiles; 9) zone of significant postdepositional dislocation of Maikop deposits; absence of continuous reflectors on provisional OGT cross sections; 10) limit of Maikop outcrops on land surface; northeastern Caucasus slope; 11) outline of area from which Maikop Formation was eroded; 12) assumed ancient land area; main source of terrigenous deposits.

[14]. The terrigenous sediments of Maikop age were transported from the northeast. Sedimentation was most intensive in mid-Maikop times when significant sand volumes were carried long distances into deep basin areas. The sediment was transported in pulses.

The sandy Maikop sequence of the eastern Precaucasus [4] indicates periodic turbidity current activity in the northern, and northeastern nearshore shelf areas of the basins. Sand and mud were deposited. Tectonism resulted in southwestward-directed slump movements of the unconsolidated sediments on the seafloor slope. Incorporation of water into slumping sediments resulted in turbidity currents. Sandy deposits settled at the toe of the continental slope. The basin, inherited from Eocene times, included the Chernolesk Basin and western Prikumsk–Tyulenevsk Arch. A series of turbidity currents subsequently filled the basin. The basin had shifted westward and each subsequent sandy layer, covering previously laid-down sand beds, was deposited successively farther basinward.

Another mechanism that formed sand layers had been described from the western Precaucasus [1]. Tectonism, reflected in erosional base level changes, introduced large terrigenous sediment volumes to the toe of the submarine slope at significant distances offshore. The deposits bypassed nearshore areas.

Not denying the importance of the first process, the high probability of an additional one should also be recognized. Data indicate that clinoform beds formed intermittently on the shelf and continuously on the slope [14]. Stream-derived sediments, introduced into the basin were carried basinward by turbidity currents and deposited on submarine fans over distances of tens-to-hundreds of kilometers. Dimensions of such an underwater process are indicated by submarine fans of the

Ganges-Brahmaputra, Amazon and Mississippi Rivers [7]. Huge amounts of terrigenous matter may be transported to a basin under favorable conditions within a short period of time. Santa Clara River, in the United States, provides an example; during the 1969 flood it carried three times its normal suspended sediment load [7].

Streams that discharged sediment volumes of tens-to-thousands of km³, for distances of tens and hundreds of km to the basin center left evidence of their existence on the Russian Platform as well. Relict fluvial channels, hundreds of kilometers long, were left by the paleo-Don River on the Platform, the largest of Tertiary streams [18, 9, 11, 19, 15, 8, 3, and others].

In the most complete reconstruction of the Oligocene–Miocene paleo-Don valley [15], that stream was traced for a distance of 1,000 km directly south from the town of Ryazan. The valley was 40–50 km wide; its depth of incision, 120 m. Early Miocene Kamennobrodsk sediments are the oldest paleo-Don deposit exposed in the Oka-Don plain land surface. The overlying Lamkinsk and Gorelkinsk Formations are of mid-Miocene, respectively, of early late Miocene age. However, the Kamennobrodsk beds are closely correlative with the Solenovsk horizon of the lower Don River [8]. According to G. I. Goretskii, the paleo-Don or the Solenovsk River was of Oligocene age. Consequently, formation of the mid-Maikop clinoform beds in the east Precaucasus were associated mostly with processes of the paleo-Don River.

The paleo-Don was traced to approximately the present latitude of Volgograd. Position of the lower course is less certain. Sparse data resulted in numerous conjectures about Miocene positions of the lower river course and the delta. Iosifova [15] placed the paleo-Don delta in the north Stavropol' area. Byrlev [3] located the lower paleo-Don in the north Caspian region. Rodzyanko [19] traced the Miocene-age paleo-Don westward, in the Azov–Black Sea Basin. This was done on the basis of field data on incised platform rivers, major fauna finds and pollen analyses. Data from publications and results of lithofacies and mineralogical–geochemical studies of middle Miocene deposits in the Precaucasus confirmed that the paleo-Don valley had shifted repeatedly [16]. The delta originally was located in the north Stavropol' area. Abrupt base level lowering in the Tarkhan and Chokrak Stages, associated with Alpine tectonism, placed the paleo-Don in a 400-m deep canyon incised in Maikop sediments that had formed along shores of the Tarkhan sea [13]. The river supplied significant volumes of sandy deposits to the Stavropol' Arch and the Belomchetsk Basin areas. Sandy deposits accumulated at this time in north Dagestan and the east Precaucasian Basin. Another platform stream, apparently the paleo-Volga, also entered the basin. In subsequent Chokrak times, rise of the south European and Donetsk Uplifts led to eastward shift of the paleo-Don in the Yashkulei area and to delta development in the northern Caspian region, near to or coinciding with the paleo-Volga course. During the second half of Karagan times the lower paleo-Don again migrated westward. Thus, at the start of middle Miocene, the paleo-Don delta was in the north Stavropol' region, while in earlier mid-Maikop times, as credibly documented, it occupied the north Caspian area.

Mineralogical and geochemical features of Oligocene–Miocene deposits of the east and central Precaucasian region in two stratigraphic type sections [17] along with composition data place paleo-Don activity in the Oka–Don plain. Mid-Miocene changes in the lower Don course [15, 16] led to two conclusions: (1) an E–W shift of the Don valley occurred in Maikop times, from the north Caspian to the north Stavropol' area; (2), an additional major platform stream, conditionally named the paleo-Volga, also existed, especially during Miocene times.

These conclusions were based on: (1) a sharp concentration increase in a number, mostly geochemically stable chemical elements in the upper Kuban' River section in the Ol'ginsk and Ritsevska Formations [17]. In contrast, in Zoramakent Formation deposits, correlatives of the Ol'ginsk and Ritsevska Formations in the Sulak River section, the concentrations of geochemically less mobile elements did not increase appreciably. Geochemical data thus indicated a silt content increase in clays of the Kuban' River section. Preexisting conditions thus had been preserved in the Sulak River section near the new sediment source.

Second, a significant admixture of silty matter in the Ol'ginsk and, to a lesser extent, the Ritsevska clay in the Kuban' River section was observed directly in thin section and samples. This is typical not only of the Kuban' River cross section but of the entire east and central Precaucasus. In addition, a N–S-oriented zone of increased sand content [12] occurred on the Stavropol' Arch during late Maikop times. Southwestward it was bounded by the Yankul'sk Ridge; on the north by the Karpinsk Ridge. The zone is 210 km long, 120 km wide; it formed in late Maikop times. Seven horizons of coarse terrigenous sediments or seven sandy siltstone beds occur in this zone. The sandy siltstone mineralogy indicated a northern land source [12]. The location of the source, the reduced thickness of the Upper Maikop beds and thinning of the terrigenous matter, along its flanks, and alternation of sedimentary matter indicate presence of a major platform stream in the Oligocene, north of Stavropol'. As shown, the paleo-Volga delta was generally located in the north Stavropol' area since the beginning of the middle Miocene [16]. At the time boundary between the Karadzhagin and Ol'gin intervals, the paleo-Don delta was located in the north Stavropol' area.

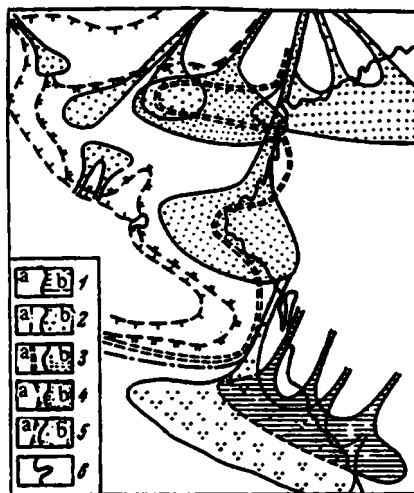


Fig. 2. Shoreline (a) and paleostream deltas (b). Northeast part of Greater Caucasus Basin [6]: 1) assumed middle-late Toarcian positions; 2) end of late Toarcian—earliest Late Aalenian; 3) late Aalenian—earliest early Bajocian; 4) early Bajocian; 5) late Bajocian—earliest Bathonian; 6) Caspian Sea shoreline.

Record terrigenous sediment transport from the Platform to the east Precaucasus occurred during the middle Maikopian. Starting in Solenovsk time, the Oligocene the paleo-Don delta was situated in the northern Caspian area. After the paleo-Volga shift north of Stavropol', deposition did not undergo marked changes in the east Precaucasus. However, the ratio of coarse detrital matter diminished greatly. Deposition of large volumes of platform sediments continued. The paleo-Volga was the sole sediment source. Indications of paleo-Volga was the sole sediment source. Indications of paleo-Volga activity in early middle Miocene, when the paleo-Don incised a deep canyon in Maikop deposits north of Stavropol', occur in north Dagestan. Unfortunately, no remnants of Oligocene—Miocene Volga valleys have yet been identified. Subsequent erosion may have completely eliminated them.

Lithofacies analysis on the central Precaucasian Maikopian showed quite widespread distribution of sandy silts in the Khadumian of the Stavropol' area. Mineralogy indicated that the terrigenous matter was derived also from the Russian Platform [10]. Khadumian sands and aleurolites are widespread. Their narrow, N—S-trending zone cuts across the Stavropol' area. Grossgeim related it to bottom current activities. The currents apparently were associated with and extended seaward of the impact area of a major platform river, apparently the paleo-Don. The Oligocene—Miocene history of the paleo-Don is the following.

Khadumian. A relatively minor uplift of the Russian Platform and regression led to increased terrigenous sediment supply by the paleo-Don to the Stavropol' area and formation of sandy—silty deposits.

Middle Maikopian. Increased tectonism in the platform abruptly activated the paleo-Don or, according to G. I. Garetskii, the Solenovskaya River. Valleys became deeply incised in the Don—Oka plains. As the river mouth shifted eastward during mid-Maikopian, a series of thick sandy layers was deposited in the eastern Precaucasus.

As indicated by N—S oriented sandy—silty zones of deposition in Ol'ginsk—Ritsevs deposits at Stavropol', during **late Maikopian** the paleo-Don returned to the central Precaucasus. Sandy—silty deposits disappeared from correlative east Precaucasian beds.

A significant **middle Miocene** regression was followed by a series of transgressions and regressions. The paleo-Volga delta shifted to the eastern Precaucasus. During Chokrak times and most of the Karagan this resulted in formation of numerous sand beds. At the end of the Karagan, the mouth of the paleo-Don shifted far westward.

Intensive avalanche sediment transport in mid-Maikop—Chokrak—Karagan times, carried large quantities of terrigenous matter from the Platform to the basins, the mouth of the paleo-Don shifted eastward to the eastern Precaucasian region. Tectonic activity declined and the volume of exported sediments tapered off. During the Khadum—late Maikop, Karagan—Konka Stages, the paleo-Don delta shifted westward to the central, even to west Precaucasian areas.

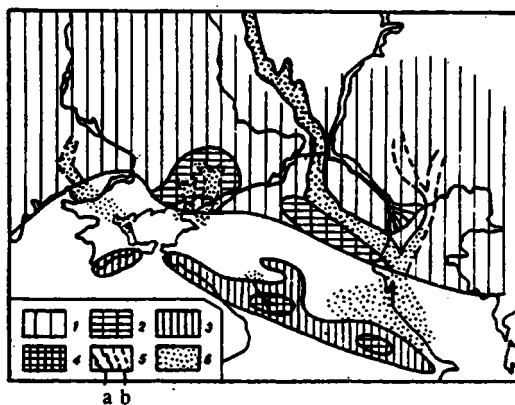


Fig. 3

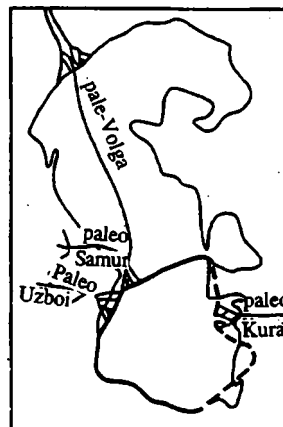


Fig. 4

Fig. 3. Paleogeography of Precaucasus area during Chokrak-Karagansk times [16]: 1) northern land area; 2) raised northern land areas; 3) Caucasian land area; 4) raised Caucasian land areas; 5) valley contours of ancient streams (a — based on data; b — assumed); 6) area of dominantly sandy matter.

Fig. 4. Map of final development stage of the Apsheron Producing Formation [2].

Judging from terrigenous mineral associations [10], the Russian Platform clearly was the main sediment source of Caucasian and Precaucasian marine areas. Terrigenous platform sediments, at least in Mesozoic-Cenozoic times, generally were transported from the north. This was not a one-time event but recurring episodes of sediment redeposition. Under favorable conditions, large volumes of detrital sediment had been quickly reworked in the geosynclinal basin.

These conditions occurred at a time when large platform river system, comparable with the modern Volga and Don was active in the region. There are two examples of massive detrital sediment transport to the southern paleobasin.

1) In Maikop times the paleo-Don delta supplied such sediments to the eastern, in part to the central Precaucasus.

2) Early and mid-Jurassic sediment transport [6] by developing large platform streams resulted in a number of extensive, very thick depocenters.

The calculated sediment accumulation rates in the central northeastern Caucasus were analyzed. This aided in the determination of the impact of the large platform streams on deposition in the eastern basins. Large sediment volumes, carried by the rivers, resulted in anomalously high deposition rates.

The authors reconstructed shoreline and delta locations of large platform streams in five consecutive time intervals (Fig. 2). They demonstrated a close relationship between transgressive-regressive shoreline shifts and delta migration. Trends of sediment accumulation rates also changed. Sedimentation was minimal on the shelf, increased on the continental slopes, at the toe of the slope and at the northern end of the basin axis.

Most terrigenous coarse sediments were carried by platform streams. The sediments bypassed nearshore shallow waters and were deposited in relatively deep basin areas, tens-to-hundreds of kilometers offshore. In intermittent, pulsating flashing, large detrital sediment volumes were transported far and deep into the basin.

3) A variety of sandstones, aleurolites and clays were deposited in the eastern Precaucasus in mid-Miocene times (Fig. 3). Detailed studies of the Chokrak-Karagansk beds of the eastern Precaucasus [16, 20] led to the conclusion that the Russian Platform was a major source of sands and clays in the eastern Precaucasus.

The paleo-Don was the major transport agent. However, terrigenous transport to the basin differed significantly from that of Maikop times.

Climoform structures in Maikop beds indicate immediate sediment export by a major stream to great distances and deep into the basin [1, 14]. Stream deposits were distributed and have accumulated over a wide area, also including prodelta and delta areas. Basin hydrodynamics, namely bottom currents played a major role in the middle Miocene in distributing and accumulating a sediment blanket [14]. The basin received primarily sandy terrigenous sediments from the river Three thousand measurements were made of cross-strata orientation [5]. These indicated that the bottom currents in the Chokrak-Karagansk times flowed from the Astrakhan sediment source toward present Grozny and Makhachkala. The current forked

into two distributaries; the Grozny current flowed westward, while the Makhachkala current moved in a south—southeasterly direction.

The bottom currents were variable. At least twenty times long periods of low hydrodynamic energy conditions alternated with period of powerful current activity. Clayey muds accumulated during the low-energy periods. Huge volumes of well-sorted, rounded sediment matter were transported far into the basin, including the south-Precaucasian areas during brief periods of intensive hydrodynamic activity. These were triggered by periodically increased tectonism, related to Alpine tectonic activity that impacted the entire Caucasus and adjacent Russian Platform areas. Tectonism also resulted in transgressive—regressive shifts of the marine shoreline. Fast and catastrophic regressions and corresponding drops in the base level of erosion incised deep platform stream valleys. The streams carried enormous volumes of mostly sandy sediments into the sea where it was carried further basinward by currents. Gradual transgression of the sea drowned stream valleys, forming huge lagoons and bays (limans) that extended far into the platform area [15]. Sandy deposits, settled in the estuaries and did not reach the marine basin where clays accumulated. Subsequent regression resulted in repeated terrigenous sediment export to the basin from the limans, their depositional sites during low levels of tectonism. This two-stage mechanism of sediment transport from the Russian Platform to the middle Miocene sea was possible under relatively shallow water conditions. Tectonic movements and changes in erosional base level increased levels hydrodynamic energy in the paleobasin and for limited periods activated powerful currents.

4) The Producing Formation was deposited during mid-Miocene in the Apsheron Peninsula. A detailed petrographic study of the peninsula and the adjacent Kabristan and Prekurinsk Lowlands, the Kubinsk, and Chelekan areas have been undertaken to determine the sediment source of the formation.

Four terrigenous mineral provinces (TMP) were identified. They are based on the different composition of the source areas. The Prekurinsk TMP (monoclinic pyroxenes and hornblendes) indicate a basin location, presently drained by the Kura River. The Kabristan—Kubin TMP included epidote, zircon, garnet, and tourmaline that reveal the Greater Caucasus Range as its source. Garnet, hornblende, and disthene are the type minerals of the Cheleken TMP. These minerals and their spatial distribution pattern point to a Transcaucasian source. The mineral composition of the Apsheron TMP (ilmenite, disthene, staurolite, and sillimanite) differs greatly from the Lesser Caucasus and Glavnyi Ridge mineralogy. A remarkable similarity was noted with Volga River mineralogy. This points to the Russian Platform as the source of the Apsheron Producing Formation. These conclusions were based on the sediment structures in this formation and their correlation with Volga and Kura deltas and prodeltas. Very thick sequences accumulated in a short time frame within two adjacent areas, the pre-Kura Lowland and adjacent Apsheron Peninsula, are characterized by different mineralogies. These were also considered in the study. V. P. Baturin concluded that the formations were deposited in the paleo-Kura and paleo-Volga deltas. The streams drained a variety of source areas (Fig. 4).

Analysis of the paleogeography and depositional conditions in the east Precaucasus and adjacent areas indicated the existence of a river, comparable in size with the Volga and Don, during the Jurassic in the Russian Platform. This stream repeatedly shifted both in east—west and south—north directions. However, in each studied instance most of the platform sediments were transported in the eastern part of the ancient sea, in the eastern Precaucasus and adjacent areas. Varying intensities of terrigenous sediment export, grain size, and maturity were due to temporal fluctuations of the erosional base level.

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BIOCHEMICAL ORIGIN OF LAYERED SILICATES WITH A GLAUCONITE-ILLITE COMPOSITION (CAMBRIAN OF NORTH VERKHOYAN'E)

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Three morphological types of layered silicates with a glauconite-illite composition, formed in the zone of diagenesis, were studied in Lower and Middle Cambrian deposits of North Verkhoyan'e. Al-glaucanites were found for the first time in Russia. It is shown that Al-glaucanite in isomorphous segregations and in the cores of chancellorid rays formed as a result of alteration of silicate material by microorganisms. A number of biomorphic nanostructures were found in the cores of chancellorid rays by means of electron microscopy.

Al-glaucanite and illite are known to be widespread in the Riphean and glauconite more commonly higher in the section, beginning in the Lower Cambrian [3, 4, 6, 7].* Various forms of glauconite occurrence have been recognized so far: globules, partial or complete replacement of mineral grains, a film around terrigenous grains, replacement of the main fine-grained matrix of the rock, fillings in internal voids in various biogenic structures, and others [6]. Biogenic fillings, directly related to organic matter, are as yet unknown for Al-glaucanite in the domestic literature. The conditions under which Al-glaucanite (as well as glauconite) is formed, and the mechanism by which these minerals fill voids in biogenic and abiogenic structures, remains largely unclear [9]. Sometimes such forms of layered silicates occur massively, and then obviously represent important sources of information on the conditions of formation of this mineral group. From the genetic point of view, it was particularly interesting to study the first known Cambrian filling (core) of a chancellorid ray composed of Al-glaucanite. The occurrence of various morphological types of Al-glaucanite together with globular glauconite was a favorable circumstance for the study of these forms.

In this article we examine in more or less detail the mineralogical nature of layered silicates that differ in color (green, white), form of occurrence (globules, cores of chancellorid rays, isometric grains), and composition (glauconite, Al-glaucanite, polymineralic forms). We also analyze the nanostructure of authigenic glauconite grains and their interaction with carbonate (organic and chemogenic) and terrigenous components of the rock. The results lead to conclusions as to their origin.

Subjects and Methods of Study. On the western slopes of the Tuora-Sis Mountains, which are part of the Kharaulakh system of northern Verkhoyan'e, Cambrian carbonate and terrigenous deposits are found along the bluffs of the Khos-Neleger River (a tributary of the Lena River in its lower reaches). The lower part of the section, corresponding to the entire Lower Cambrian and the Amgaian stage of the Middle Cambrian, is subdivided into two suites: the Tyuser and Sekten [5]. The Tyuser suite is composed of variegated siltstones, argillites, limy mudstones, and argillaceous limestones that vary in color (red, gray green). Redbeds decrease upward in the section. The suite, 133 m thick, contains numerous fossils that can be assigned to the Tommotian and Atdabanian stages of the Lower Cambrian. The Sekten suite is composed of gray and greenish-gray limestones 105 m in thickness. It also contains various fossil forms and is assigned to the upper part of the

*In the present paper we use the terminology recommended by the International Committee on Nomenclature and used in [8], in which glauconite contains $\text{Fe}^{3+}_{\text{VI}} > \text{Al}_{\text{VI}}$, the unit cell parameter $b > 9.06 \text{ \AA}$, the degree of iron content is $n(\text{Fe}^{3+}/\text{Fe}^{3+} + \text{Al}) > 0.5$; in Al-glaucanite $\text{Al}_{\text{VI}} \geq \text{Fe}^{3+}_{\text{VI}}$, $b < 9.06 \text{ \AA}$, $n = 0.5-0.25$; in illite $\text{Al}_{\text{VI}} > \text{Fe}^{3+}_{\text{VI}}$, $n < 0.25$.

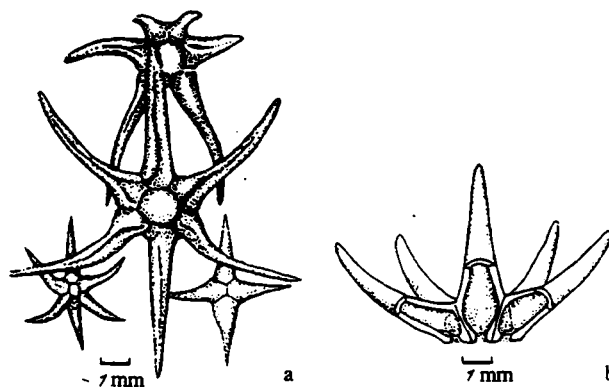


Fig. 1. Chancellorid rosettes (a) and a section through a rosette (b).

Reconstruction by A. Yu. Zhuravlev.

Lower and lower half of the Middle Cambrian (Botomian and Amgaian stages). Individual beds in both suites include glauconite grains as well as glauconitized cores of chancellorids. Samples were collected by Ushatinskaya from the lower part of the Tyuser suite (sample 4a) and in 10 m of section in the upper part of the Sekten suite (sample 3d) from rusty-brown and gray limestones, respectively.

We briefly consider the nature of the chancellorids. Small skeletal remains (1-2 mm, rarely to 5 mm) are commonly found in Cambrian rocks, and have the form of either isolated cup-shaped rays or rays in star-shaped rosettes of two, three, or more fragments (Fig. 1a). They were first described by Walcott [13] from the Middle Cambrian; he named them *Chancelloriidae* and referred them to the sponges because of their spicules. It is now widely accepted that the rays and rosettes are sclerites, i.e. detached parts of the skeleton of some problematic form in which they may have served as a protective cover [1, 10]. Individual rays are thin-walled, hollow forms extending outwards from the center (Fig. 1b). The calcite walls are about 10 μm thick. According to Bengtson and others [10], the original skeletal material of the chancellorids may have been aragonite. The spicular walls rarely survive extraction from the rock, especially if it is a carbonate rock that is dissolved in acid. In such cases the core is studied, and shows the inner surface of the rays. The core may be composed of glauconite or fine clay which probably filled the hollow ray after the death of the organism, or in some cases calcium phosphate with a distinct spherulitic structure. During life organic tissue was probably present in the interior of the ray [10].

Minerals for study were selected under the binocular microscope from the residues after treatment with 6-8% acetic acid. These insolubles included, in addition to glauconite and phosphatic brachiopod shells, a large amount of isomorphous, porous, white (sample 3d) and rusty brown (sample 4a) silicates. The rusty color was produced by iron oxide, but in some parts of the rock and in some shells the silicates retain their white color. Significantly, white silicates have also filled hollow chancellorid rays and other pore spaces in various fossils. This is particularly apparent in the study of cleavage or fracture surfaces etched with 2% HCl.

The light-gray and rusty-colored rocks are highly fractured, with the fractures filled with coarsely crystalline, white calcite. The calcite veins cut across globular glauconite and glauconite fillings in chancellorid rays, as well as various clusters of white silicates. This indicates that the carbonate was introduced after the rock was lithified.

Three samples were selected for detailed mineralogical study: 1) green globules (sample 4a), 2) green cores of chancellorids (sample 3d), and 3) porous white isomorphous material in the fine-grained carbonate matrix of the rock (sample 3d). A combination of studies was carried out: optical, with the scanning electron microscope, as well as chemical analysis, diffractometry, microprobe, (Link-860; Camebax), and infrared spectrometry. Examination by scanning electron microscope in conjunction with microprobe analysis (Link-860) was conducted in the Paleontological Institute, while the other analyses were carried out in the Geological Institute of the Russian Academy of Sciences.

Nature of the Layered Silicates. Globular layered silicates were typical of the rusty-brown limestones (sample 4a), where they are basically palmate, pithy, rounded, and nodular in form. The center of the globule is light to dark green, while the periphery is rusty-reddish; it has a microaggregate extinction. The many fractures in the globule are filled with calcite crystals and (or) iron oxides. The latter, like the calcite, commonly replaces the globule both in the periphery and interior. The maximum grain size is about 1 mm, but most grains are no larger than 0.5-0.25 mm. They are irregularly distributed in

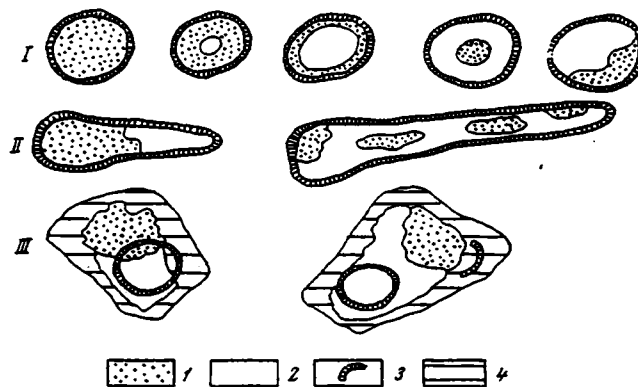


Fig. 2. Relationship of Al-glaucanite and white silicate material in the cores of cancellorid rays. I, II) Transverse and longitudinal sections of cores, respectively; III) cores in limestone matrix (sample 3d). 1) Al-glaucanite; 2) white silicate material; 3) carbonate shell of rays; 4) limestone matrix.

the rock, and are concentrated in areas of shell fragment accumulations. In hand specimens, globule zones form a complex picture of indistinct twisting and turning bands. In some areas the globule zones are cut by bioturbation structures.

The green cores of the cancellorid rays are found mostly in gray shelly limestone (sample 3d), where their size depends on the size of the hollows in the rays, and is usually no greater than 1-3 mm. Upon etching, the surfaces of the cores commonly show the imprint of coarsely crystalline calcite, as well as some thin Fe-hydroxide films.

Cores composed of white silicate material were quite commonly found in the rocks studied. These sometimes include small, blurry, greenish specks, and in a few cases the green fades into white within a single core. Cores were found that were green on the outside and white in the center. Fig. 2 shows all the various relationships of green and white silicate material found in the cores. Color variations in the cores vary chaotically and do not form conspicuous segregations or zones of concentration.

In addition to the cores, white silicate material is found in isomorphic segregates located both chaotically and in layers in the fine-grained limestone matrix. Locally they form pale green patches (Fig. 3, sample 3d). Here molds reflecting the fine sculpturing of the inner and outer surfaces of shells are formed in zones of high concentrations of the silicate material.

Nanostructures in Various Segregates of Layered Silicates. The scanning electron microscope revealed aspects of the nanostructure of various forms and colors of layered silicates and made it possible to establish their relationship to carbonate material in the rocks. The differences in the relationship of green and white cancellorid cores with the calcite matrix have been noted. With a slight increase in size, the green cores have sharp, smooth shapes (Fig. 4a, b). In many cases a border zone up to 10 μm wide composed of globular iron hydroxides occurs at the boundary with the matrix. The border zone is cut by round channels (about 1 μm across) normal to the surface of the core. Cores composed of white silicate material have packets and individual plates of layered silicates that have intruded between calcite crystals in the zone, which can be assumed to be the wall of the ray.

The contact between the globules and the fine-grained calcite matrix is sharp. Coarse idiomorphic calcite crystals are commonly present within the globules. A typical glauconite nanostructure of thin, curved flakes (or petals) with smooth, sometimes rounded, edges can be easily seen in the green globules (sample 4a). Such nanostructures, forming aggregates of flakes gathered into bunches, are present everywhere, looking like heads of cabbage, fans, rooster tails, and so on (see Fig. 4c).

Nanostructures in layered silicates that occur in the green and white cores of cancellorid rays are generally quite similar (sample 3d). They are a variety of platelets and packets (sometimes quite numerous) that occupy the area between idiomorphic crystals of calcite. The platelets typically have a rounded or locally scalloped shape (see Fig. 4d). Individual platelets range from 97 to 290 nm in thickness. A foliated structure, reminiscent of mica plates, can often be seen on the surface of the platelets. Calcite crystals are also an important component of the cores. Calcite crystals are characteristically larger within the cores and at their surface than in the surrounding matrix, and are usually idiomorphic. Calcite in the matrix

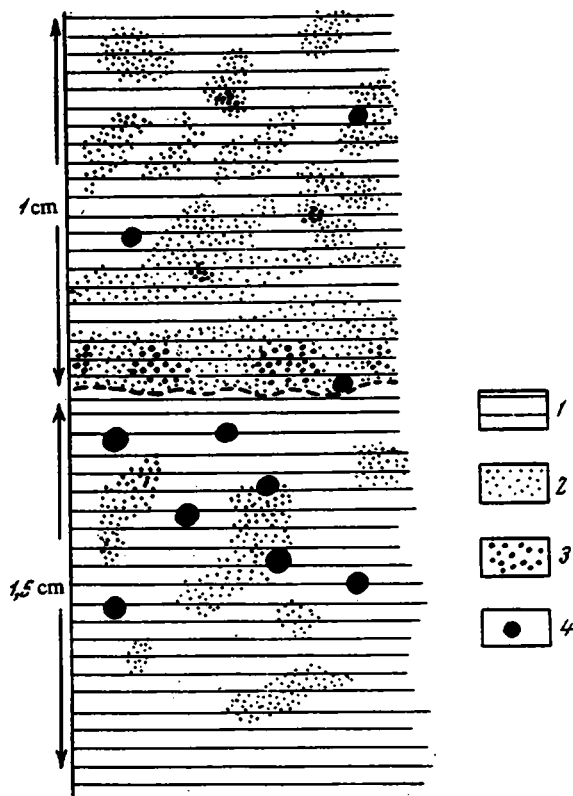


Fig. 3. Distribution of white silicate material in limestones (sample 3d). 1) Limestone matrix; 2) white silicate material; 3, 4) Al-glaucoune in the matrix and cores of cancellorid rays, respectively.

forms complex aggregates of intergrown crystals. Generally in the cores the calcite crystals are completely or for the most part are isolated from each other by a fringe of silicate material. Upon solution of the calcite, replicas of the crystal surfaces can be seen as fine sculptures in the silicate platelets.

Study of the green silicate material in the ray cores reveals areas composed of a dense, cryptocrystalline material with typical biomorphic nanostructures (see Fig. 4e, f). The platy structure of the silicate material in these areas is not very clear. The platelets and packets have a soft, rounded shape. The contact with idiomorphic crystals of calcite is sharp. The following morphological types can be seen among the biomorphic structures: 1) pellets, isolated or combined in an extended structure; 2) elongated bodies, round in cross section, branching, with thin, rounded ends; 3) curving, vermiform bodies, also round in cross section, sometimes distinctly sectional. The latter type is most common, and forms large areas of the cryptocrystalline material in the cores. The biomorphic structures vary widely in size. The rounded bodies average 63 nm across, but there are large round and cocoon-shaped forms that are 1 μm and more in length. The elongate bodies reach 2 μm in length with a maximum thickness of 300 nm.

The biomorphic structures, rarely encountered in the white silicate material, are ball-shaped bodies with smooth surfaces. They range in size from 1 to 4 μm . Sometimes their surfaces are coated with fine platelets of silicate material. A large, elongate organic clast (more than 30 μm long) was found to be replaced by silicate material. By its large size it is apparent that the silicate platelets have the same orientation throughout the clast, lie closely together, and have a clearer shape than in the surrounding carbonate matrix.

Diffraction Data. X-ray and electron diffraction studies of the globules (sample 4a) and green cores of rays (sample 3d) showed the following. Oriented samples of the grains on diffractograms revealed a micaceous mineral with essentially no expanded layers ($\leq 10\%$). Chlorite and quartz traces are noted in sample 3d. An oriented sample of grains for the area of d (060) produced a reflection for d at 1.508 Å, which is characteristic of Al-glaucoune ($b = 9.048$ Å). For sample 4a in this area the reflection for d was 1.514 Å, which corresponds to true glaucoune ($b = 9.08$ Å). X-ray analysis of the white material in isomorphic segregations and cores of rays demonstrated its polyminerale composition. In addition to layered

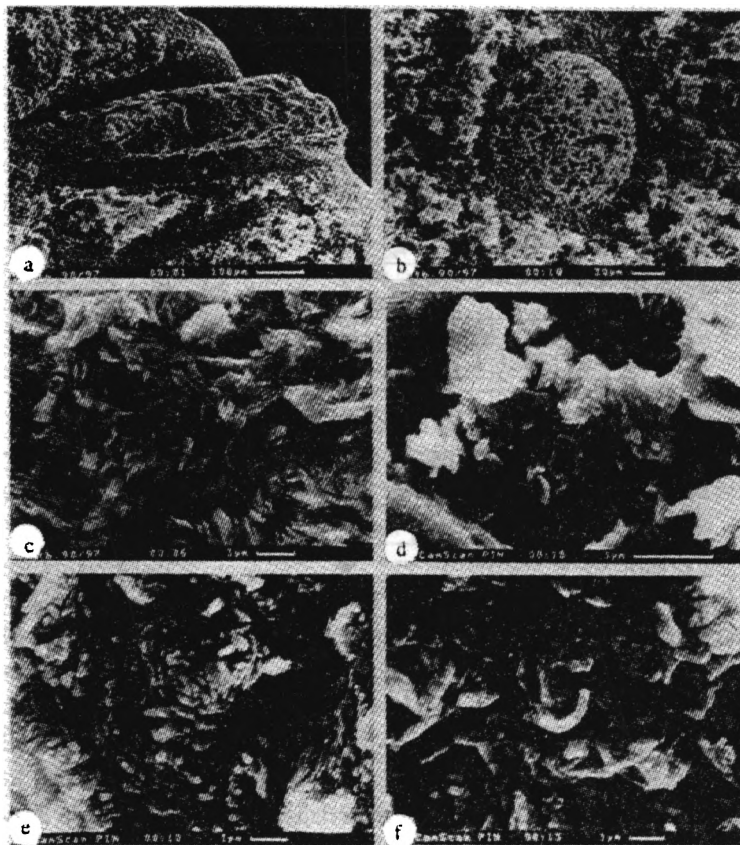


Fig. 4. Nanostructures in layered silicates. a) Core of a chancellorid ray composed of white (in the center) and green (on the margin) silicate material (Al-glaucanite); b) cross section of a core composed of Al-glaucanite (with areas of isomorphic white silicate material in the carbonate matrix); c) nanostructure of globular glauconite (sample 4a); d) nanostructure of Al-glaucanite in the core of a chancellorid ray; e, f) biomorphic structures in the core of a ray composed of Al-glaucanite (e, aggregate of fine globules; f, vermiform structures).

silicates, mica and chlorite, they contain a significant amount of quartz, and as an accessory mineral, feldspar. The micaceous mineral, judging by the parameter b (9.036 Å), is Al-glaucanite (Fe-illite) or illite, and the chlorite ($b = 9.25$ Å) is an Fe, Mg variety.

Chemical Composition. A complete silicate microanalysis was carried out for the green grains in samples 4a and 3d (Table 1). The first sample, as previously noted, is mainly globular material with a small amount of chancellorid cores; the second sample is the opposite: mostly cores, with globules being sparse. These and other grains were examined in the scanning electron microscope, along with study of the qualitative distribution of petrogenic elements in individual points and areally (Link-860 microprobe) (Fig. 5a-c). X-ray spectral analysis (Camebax microprobe)* was completed for 9-12 grains in each sample. Qualitative microprobe studies were also carried out for: 1) isomorphic white and green segregates in the carbonate matrix (see Fig. 5d, e), 2) a white chancellorid core (see Fig. 5f), and 3) made up of an outer green part and inner white silicate material (see Fig. 4a and 5g, h).

*X-ray spectral analysis on the Camebax microanalyzer by G. V. Karpova, Geol. Inst., Russian Acad. Sci.

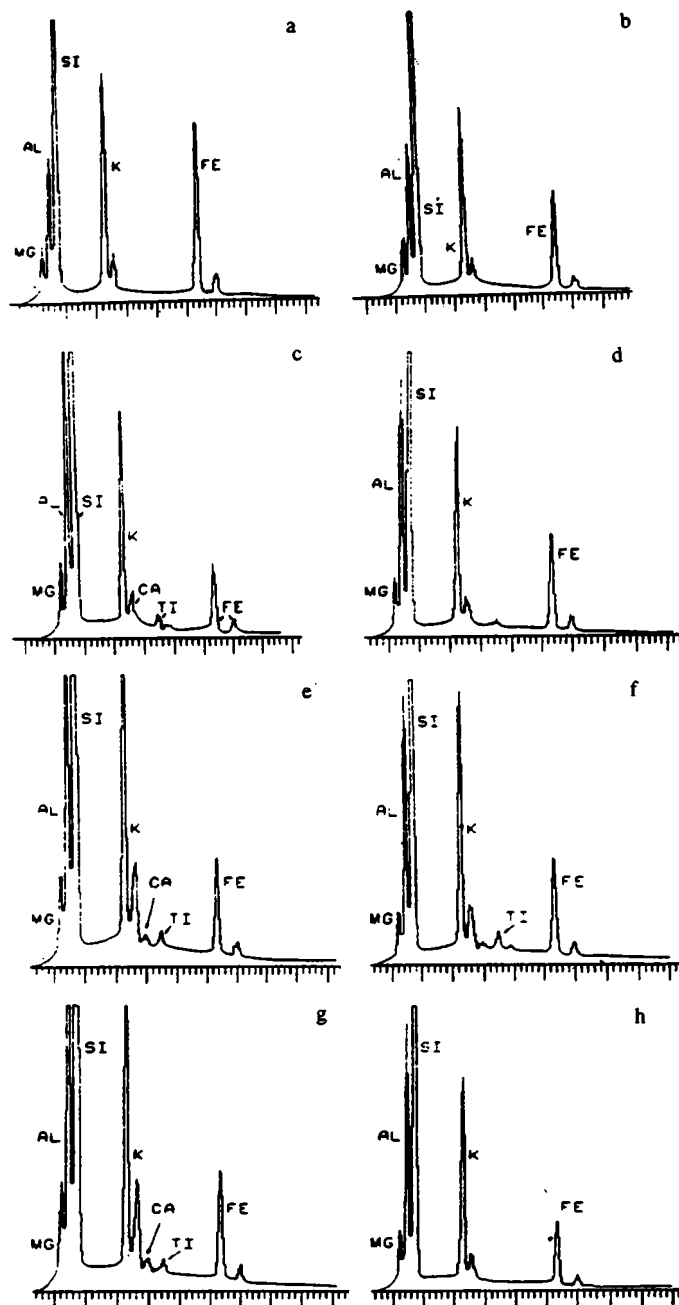


Fig. 5. Relationship of petrogenic elements in layered silicates. a, b) Globules (a, sample 4a, b, sample 3d); c, d) layered silicates of different colors (c, cores of cancellorid rays composed entirely of Al-glaucanite; d, isomorphous segregate of Al-glaucanite in limestone matrix; e) white isomorphous material in limestone matrix; f) core composed entirely of white silicate material; g, h) composite core (g, interior white zone; h, outer green (see Fig. 2 and 4a).

Crystallochemical formulas of the samples (Table 2) were calculated from the chemical analyses of the silicates based on the assumption of a stable ionic composition of $[\text{O}_{10}(\text{OH})_2]^{-22}$. As can be seen from the Table, the samples differ in the basic ratio of Fe^{3+} and Al in the octahedral position of the 2:1 layer. In sample 3d, Al is predominant, and in sample 4a the Fe^{3+} content somewhat exceeds Al. The iron content n is 0.30 and 0.52, respectively. According to [8], the iron content of the minerals is consistent with glauconite (sample 4a) and Al-glaucanite (sample 3d). The size of the octahedral charge in the samples is 0.41 and 0.32, respectively; in the first sample it is close to tetrahedral, while in the second, it is somewhat lower.

TABLE 1. Chemical Composition of the Samples, %

Sample No.	Grain size mm	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O ⁺	H ₂ O ⁻	Total
3d	0,4–0,1	50,80	0,05	16,23	7,95	3,85	–	4,84	0,23	7,64	6,49	1,70	99,78
4a	0,63–0,315	50,73	None	13,54	14,80	1,90	–	3,49	0,15	8,59	4,59	1,71	99,50

Note. Calculated admixtures, %: Sample 4a – Ca₃(PO₄)₂ 0,70; CaCO₃ 2,01; MgCO₃ 0,46; Sample 3d Ca₃(PO₄)₂ 0,26; CaCO₃ 1,68.

TABLE 2. Crystallochemical Formulas of the Minerals

Sample No.	Grain size mm	Cations								Iron content, n	Charge		
		Tetrahedral		Octahedral			Interlayer				Tetrahedral	Octa- hedral	Inter- layer
		Si	Al	Fe ³⁺	Al	Fe ²⁺	Mg	K	Na				
3d	0,4—0,1	3,62	0,38	0,42	0,98	0,23	0,52	0,69	0,03	0,30	15,62	5,68	0,72
4a	0.63—0.315	3.60	0.40	0.79	0.74	0.11	0.39	0.70	0.02	0.52	15,62	5,59	0,72

TABLE 3. Results of Microprobe Analysis, %

Sample No.	Occurrence	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
3d	Chancellorid cores	52,51	0,12	14,91	10,36	7,13	0,16	0,03	8,86
		51,35–54,18	0,07–0,2	13,77–16,72	8,94–12,01	6,20–7,80	0,1–0,25	0,006–0,06	8,75–9,01
4a	Globules	50,36	0,03	9,56	19,57	4,59	0,13	0,02	9,29
		48,96–51,39	0,015–0,075	7,66–11,70	16,95–21,35	4,42–4,76	0,01–0,25	0,002–0,06	9,17–9,49

Note. Numerators are the average values for 12 (sample 4a) and 9 (sample 3d) points; denominators indicate range.

The total charge of the 2:1 layer is quite high (0.72) and is compensated by interlayer cations K (0.70; 0.69), along with which the cations Na and possibly Mg are present in minor amounts (sample 3d).

Microprobe (Camebax) analysis generally confirms the cation relationships in the minerals (Table 3), but compared to the results of a complete silicate analysis they give low values for Al_2O_3 and high values for MgO, SiO_2 , and K_2O ; whereas the total Fe content may be either increased or decreased.

Comparing the results of qualitative analysis obtained on the Link-860 microprobe for glauconite globules (sample 4a) and the Al-glauconite cores of cancellorid rays (sample 3d), all of the subjects of study may be subdivided into three groups with respect to the Al and total Fe content (see Fig. 5). The first group consists of glauconite globules, which are present in both samples (see Fig. 5a, b). They are characterized by an Fe content equal to or appreciably greater than Al. The second group consists of green layered silicates that make up the cores, and green isomorphic segregates in the carbonate matrix (see Fig. 5c, d, h). The layered silicates of this group are close to Al-glauconite in the relationship of the cations Fe and Al. As for the white silicate material, which is placed in the third group even though it occurs in the cores or is distributed through the carbonate rock as isomorphic segregates, Al is always found to far exceed Fe (see Fig. 5e-g). Moreover, in comparison to the two previous groups, titanium is persistently detected at the level of sensitivity of the sampling. In this connection it is important to consider the content of this element in the subjects of the study. According to the total silicate analysis (see Table 1), in the glauconite TiO_2 is either undetected or occurs in extremely small amounts (sample 3d). In an attempt to improve these data using the same method but with larger portions, the TiO_2 content in these samples increased to 0.11 and 0.21% respectively. The TiO_2 content in the cores thus proved to be greater than in the globules, which was also found in the results of the microprobe studies (see Table 2). In the same samples, but in the rusty-brown (sample 4a) and white (sample 3d) silicate material rather than in the glauconites, the TiO_2 content was even higher (0.22 and 0.83%, respectively).

Infrared spectroscopy of the green grains (samples 3d, 4a) and the white silicate material (sample 3d) was conducted in the valence range of the OH group. The results clearly show the ratio of Al and Fe in the mineral structure, and confirm the findings of the chemical studies. Thus, for the high Al subjects in sample 3d (green cores and white material) a strong band was determined with a maximum at about $3600\text{--}3580\text{ cm}^{-1}$ (AlFe^{2+} , AlMg), while the more iron-rich globules in sample 4a had a broad spectrum with two weak maxima in the area of $3515\text{--}3540\text{ cm}^{-1}$, as a result of various combinations of the cation pairs ($\text{Fe}^{2+}\text{Fe}^{3+}$, $\text{Fe}^{3+}\text{Fe}^{3+}$).

Discussion of Analytical Data. Globular layered silicates in the study set were Fe-dioctahedral micas: glauconite with a content of 0.79 units of $\text{Fe}_{\text{VI}}^{3+}$ and $0.74 = \text{Al}_{\text{VI}}$; iron content $n = 0.52$, and a parameter $b = 9.08\text{ \AA}$. The green cores of cancellorid rays are composed of Al-glauconite ($\text{Al}_{\text{VI}} = 0.98$, $\text{Fe}_{\text{VI}}^{3+} = 0.42$ units; $n = 0.30$; $b = 9.048\text{ \AA}$). Chlorite and quartz are present as minor admixtures. The mica in isomorphous green segregates has a similar composition, while the white silicate material (in cores and in the rock matrix) there is more aluminum and the mineral is apparently illite ($\text{Al}_{\text{VI}} \gg \text{Fe}_{\text{VI}}^{3+}$; $b = 9.036\text{ \AA}$), with a little chlorite, quartz, and feldspar present.

On the basis of the data obtained it is possible to arrive at certain conclusions as to the formation of Al-glauconite during diagenesis as a result of the alteration of terrigenous silicate material. Three morphological types of layered silicate of different compositions were studied and observed in the rocks. All of these were taken from limestones in which terrigenous components occurred as finely dispersed polymineralic material (mica, chlorite, quartz, feldspar). In the Tyuser suite, which includes siltstones and argillites in addition to limestone, glauconitic globules are the dominant morphological type of these silicates (first type). Al-glauconite is rarely found in the cores of cancellorid rays here. In contrast, in the Sekten suite, composed entirely of limestone, cores composed of Al-glauconite (second type) are predominant, and Al-glauconite globules are quite rare. These limestones also contain patches of replacement of white terrigenous silicates by green, the third morphological type of occurrence of Al-glauconite. There is no principal genetic difference between the second and third types. In this and other cases it developed in finely dispersed terrigenous material. This is supported by the fact that a considerable part of the cores of rays are composed of white silicate material only, which is polymineralic and includes not only finely dispersed particles but also fine silt, which under the scanning electron microscope was found to include isometric, angular quartz grains. Moreover, numerous cores were noted in which the white silicate material was only partly, in patches, replaced by Al-glauconite. The primary filling of the hollow rays with pelitomorphous terrigenous material and its subsequent replacement by Al-glauconite clearly proves to be an example of a concentric zonation of replacement, in which the outer part of the core is Al-glauconite and the inner is white, polymineralic silicate material (see Fig. 4d and 5g, h).

The nature of the interrelationship of the abundant segregates of globular glauconite and the rare Al-glauconite cores in the Tyuser limestones (sample 4a) is unclear, however. The contact between the finely dispersed terrigenous material in the matrix of the limestones and the globular glauconite is always sharp and clear, ruling out replacement of the first type. It

is also noted that the globular segregates seen in the Sekten suite are intermediate in the ratio of Al to Fe between Al-glaucanites of the cores and globular glauconite in limestones of the Tyuser suite. Considering the large role played by illite in the terrigenous material of the limestones, it is suggested that the chemical composition of the original material played an important part in the formation of the Al-glaucanite in the cores and the associated globular segregates of layered silicates (sample 3d). On the other hand, the effect of the terrigenous components in limestones was insignificant with respect to the formation of the globular glauconites (sample 4a). Recalling that the Tyuser limestones contain a large amount of iron oxides not involved in the lattices of terrigenous minerals, it is possible that a large amount of dissolved iron in the muddy bottom waters was the main cause of alteration in this suite to the more iron-rich glauconite.

Chemical analyses attest to the fact that alteration of terrigenous material, its replacement by Al-glaucanite, was determined by appearance in very small areas of very specific conditions that were favorable for the migration of a number of elements, including such poorly mobile elements as titanium. Where the cores have been glauconitized the TiO_2 content is markedly lower than in the terrigenous silicate matter. How did such condition arise so rapidly in the hollow cores of the cancellorid rays? One possibility may be intensive, very local microbial activity that set up the conditions for Al-glaucanite formation. As noted earlier, during life the cores were filled with organic tissues that probably served as a favorable site for microorganisms after the death of the animal.

At the present time there is no doubt as to the primary gel nature of the glauconite [3]. Silicate gel formed as a product of the breakdown of polymineralic pelitomorphous terrigenous material under the catalytic effect of microorganisms and could easily fix in place (fossilize) bacterial colonies. The biogenic structure could hardly survive recrystallization of the colloid, however. In actual fact, the crystalline nature of the Al-glaucanite was quite obvious in most of the cores examined during the study of the nanostructures, and a few types of biomorphic structures could be found only in cryptocrystalline areas [11]. The observed replacement of megafossils by Al-glaucanite also attests to the participation of microorganisms in the alteration of terrigenous silicate material.

The concept of glauconite formation by the action of microorganisms was expressed by V. I. Vernadskii some 60 years ago [2]. No direct evidence of the presence of bacteria in glauconites has yet been found, however. Glauconite nanostructures similar in size and morphology to those we found have been reported in [12], but they were simply called vermiculitic particles without specifying any origin. We believe that the close paragenetic association of biomorphic structures with various biogenic remains is a convincing argument for the active participation of microorganisms in the formation of Al-glaucanite.

The following points are emphasized in conclusion.

1. Three morphological types of occurrence of glauconite—illite layered silicates have been observed in the Lower-Middle Cambrian Tyuser and Sekten suites of Northern Verkhoyn'e: globules, cores of cancellorid rays, and isolated segregations in the carbonate matrix of limestones. Glauconite occurs mainly as globules, Al-glaucanite as cores and in isomorphous green segregations, and illite in these two morphological types, but as a white mineral. It is of interest that this is only the second discovery of Al-glaucanite in Cambrian deposits. A mineral of this composition has been found previously only in Middle Cambrian rocks of southern Sweden, where it also filled biogenic and abiogenic voids in sandstones and siltstones [9].

2. All three morphological types of glauconite—illite layered silicates were formed in the zone of diagenesis, and Al-glaucanite in the cores of cancellorid rays and in isomorphous segregations as a result of alteration of terrigenous silicate material.

3. The discovery of several types of biomorphic nanostructures in Al-glaucanites, first reported here, suggests the participation of organic material in the formation of glauconite—illite minerals, and thus their biochemical origin.

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GEOCHEMICAL FEATURES AND CONDITIONS OF FORMATION OF CARBONACEOUS ROCKS OF THE UL'DZIT-GOL' COMPLEX OF CENTRAL MONGOLIA

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In the article, we present the results of investigations of carbonaceous rocks of the Ul'dzit-Gol' complex of Lower-Middle Riphean in Central Mongolia. In terms of chemical composition, rocks investigated form a complete sedimentogenic series: sandstone-clay-carbonate, with the greatest content of C_{org} characteristic of essentially clayey rock. On the basis of the data obtained, we reconstructed the composition of the rocks of the source area, the mineral compositions of the original deposits, and the salinity regime of the sedimentary paleobasin.

The study of lithogenesis during early stages in the Earth's geological history is of great scientific and practical value. For this reason, carbonaceous rocks, packets, and formations which accumulated over the entire Precambrian and which are found in association with many commercially valuable minerals (gold, uranium, lead, zinc, graphite, shungite, etc.) occupy a position of special importance among sedimentary-metamorphic deposits. Moreover, study of carbonaceous deposits is needed because of the direct relevance of such rocks to the problem of the formation of the Earth's first fuel minerals and the problem of the evolution of organic matter over the Earth's geological history. Thus, a comprehensive study of Precambrian carbonaceous deposits and their conditions of formation is one of the most important tasks in Precambrian geology.

Mongolia is one of the regions where Precambrian carbonaceous rocks ("black shales") occur. Within the composition of the Precambrian here, we can identify Pre-Riphean (Archean and Lower Proterozoic), Riphean, and Vendian deposits. These deposits are most widely occurring in the northern and central parts of Mongolia. It should be noted that carbonaceous rocks can be identified within all chronological subdivisions of the Precambrian, beginning with AR_2-PR_1 [1, 4, 7, 12, etc.).

The western part of the Bayan-Khongorsk structural zone of the Caledonides (the so-called Baydarik block of the Precambrian) is a region within Central Mongolia where carbonaceous deposits widely occur. Here, Precambrian formations can be subdivided into three chronological complexes: the Baydaraginsk (AR_2), with an absolute age of 2650 ± 30 m.y. as determined by the U-Pb-method based upon zircon in tonalite gneiss; the Bumbugersk (PR_1), with an absolute age of 1900-2000 m.y. as determined from zircon in granitoids; the Ul'dzit-Gol' (R_{1-2}), dated on the basis of fauna [6, 10, etc.]. The oldest carbonaceous rocks occur within the composition of Bed II of the Bumbugersk complex, where they are represented by garnet-biotite schists and kyanite-staurolite-garnet schists frequently containing substantial quantities of carbonaceous matter [6, 16]. According to recent data [8], this rock complex (an analog of the high-alumina Kiev series of the Baltic Shield) can be traced in the form of isolated outcrops over large distances in Central and Western Mongolia.

In this report, we will discuss carbonaceous rocks at the next age levels, the Lower and Middle Riphean (Ul'dzit-Gol' complex). At these levels, carbonaceous are more widely occurring than in the lower-lying Bumbugersk complex of the Lower Proterozoic.

Our report contains original data obtained from samples of carbonaceous rock collected during field work in Central Mongolia. Analytical determinations (contents of petrogenic oxides, minor and trace elements in sample and monofractions of pyrite) were carried out in the chemical laboratory of the Institute of Geological Sciences of the Russian Academy of Sciences; quantitative spectral analyses of monofractions of carbonaceous were performed at the Institute of Geological Sciences, Ukrainian Academy of Sciences.

Geological Institute, Russian Academy of Sciences, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 92-100, January-February, 1994. Original article submitted May 19, 1992.

TABLE 1. Average Contents (in denominator) and Ranges of Variation (in numerator) in Chemical Composition of Carbonaceous Rocks of the Ul'dzit-Gol' Complex, wt. %

Rock	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO
Alumini-ferous shales (16)	<u>50.43-60.82</u> 57.35	<u>0.95-1.51</u> 1.18	<u>18.64-24.63</u> 21.02	<u>0.99-7.96</u> 4.13	<u>0.88-4.97</u> 2.90	<u>0.00-0.08</u> 0.026
Quartz-mica schists (13)	<u>53.66-68.78</u> 64.51	<u>0.64-1.84</u> 1.17	<u>11.73-17.77</u> 16.04	<u>1.47-21.25</u> 4.80	<u>0.27-3.74</u> 2.55	<u>0.00-0.33</u> 0.076
Quartzites (7)	<u>71.51-91.84</u> 81.93	<u>0.30-0.92</u> 0.52	<u>00.00-12.65</u> 6.04	<u>1.23-7.00</u> 3.50	<u>0.24-5.27</u> 1.35	<u>Сл.-0.07</u> 0.013
Carbonate content of schists (average of 10.2% CO ₂) (3)	<u>38.92-66.51</u> 52.02	<u>0.37-0.81</u> 0.61	<u>2.92-14.22</u> 8.96	<u>2.08-4.72</u> 3.00	<u>1.93-3.27</u> 2.43	<u>0.09-0.13</u> 0.110

Rock	CaO	MgO	Na ₂ O	K ₂ O	S _{total}	C	P ₂ O ₅
Alumini-ferous shales (16)	<u>0.55-3.18</u> 1.14	<u>0.28-2.59</u> 1.72	<u>0.45-2.37</u> 1.32	<u>2.27-4.77</u> 3.36	<u>0.01-0.70</u> 0.048	<u>0.19-3.50</u> 1.20(15)	<u>0.00-0.21</u> 0.056
Quartz-mica schists (13)	<u>0.48-4.31</u> 1.61	<u>0.21-2.07</u> 1.14	<u>0.34-3.36</u> 1.13	<u>0.23-5.07</u> 3.00	<u>0.00-0.96</u> 0.1446	<u>0.00-0.87</u> 0.4346	<u>0.00-0.39</u> 0.1187
Quartzites (7)	<u>0.46-2.26</u> 1.25	<u>0.00-3.83</u> 1.10	<u>0.11-0.68</u> 0.28	<u>0.31-2.44</u> 1.11	<u>0.00-0.02</u> 0.004	<u>0.42-1.02</u> 0.69	<u>0.00-0.19</u> 0.077
Carbonate-containing schists (average of 10.2% CO ₂) (3)	<u>5.74-26.90</u> 16.02	<u>1.06-1.76</u> 1.40	<u>0.22-0.68</u> 0.49	<u>0.31-2.44</u> 1.51	—	<u>0.54-0.85</u> 0.74	<u>0.01-0.16</u> 0.08

Explanation. Numbers of samples are given in brackets. The analyses were performed in the analytical-chemical laboratory of the Institute of Geology, Russian Academy of Sciences (E. V. Cherkasova and M. N. Rudenko, analytical chemists).

THE UL'DZIT-GOL' COMPLEX (R₁₋₂) OF CENTRAL MONGOLIA

Within the Ul'dzit-Gol' complex, carbonaceous material C_{org} is present in rocks of the entire sedimentogene series (an idealized facies profile): fragmental-clayey-carbonate rock. The grey-dark grey color of the rocks can be partially explained by the pigmenting effect of biogenically derived carbonaceous material. Evidence for a biogenic origin of C_{org} includes finds of stromatolites (*Conophyton garganicus* Kor.), oncolites, fragments of organic films, and filamentous algae [2, 10]; i. e., we did not find the "separation" of C_{org} from the remains of its "producers" (very simple organisms) that is found in the vast majority of cases involving Precambrian rocks.

A 4-m basal layer of gravelstone and coarse-grained sandstone lies at the base of this complex. Light grey-grey dolomite (CaO 25.92-31.60%; MgO 17.56-21.55%; CO₂ 38.65-45.60%; based upon 6 samples) lies conformably on the basal layer. There is a 25-30 m layer of mixed quartzite (SiO₂ ~98%) among the dolomite. Higher along the section, there are metapelitic carbonate-quartz schists (SiO₂ 49.97-66.64%). Low contents of MnO (0.18%) and S_{total} (<0.04%) are characteristic features of these schists; a predominance of K₂O over Na₂O is also typical. In turn, these schists are overlain by a stratum (20-35 m) of bituminous limestone showing all shades of grey coloration. Quite frequently, the limestones are,

TABLE 2. Average Normative-Mineral Compositions of Rocks of the Ul'dzit-Gol' Complex

Components of parent rocks		Aluminiferous shales (16)	Quartz-mica schists (13)	Quartzites (7)	Carbonate- containing schists (3)
mineral groups	minerals	1	2	3	4
Clastic	Quartz	19,42	37,95	72,86	38,39
	Plagioclase	6,77	9,25	1,78	3,96
	Orthoclase	0,98	2,14	1,03	—
	Total	27,17	49,34	75,67	42,35
Clay	Kaolinite	6,86	6,50	1,85	1,81
	Hydromica	28,02	22,69	7,64	12,14
	Montmorillonite	24,78	7,05	2,94	2,18
	Chlorite	1,63	2,02	4,71	6,94
	Serpentine	—	0,12	0,19	—
	Total	61,29	38,38	17,33	23,07
Oxides	Goethite	3,61	2,07	2,16	—
	Pyrolusite	—	0,05	—	—
	Total	3,61	2,12	2,16	—
Carbonate	Dolomite	0,07	0,43	0,51	1,50
	Calcite	—	—	0,47	24,50
	Siderite	1,24	2,65	—	—
	Ankerite	3,91	4,83	2,47	6,98
	Rhodochrosite	—	—	—	0,12
	Total	5,22	7,91	3,45	33,10
Minerals of Ti, P, etc.		2,77	2,34	1,39	1,48

Explanation. Probable types of original deposits: 1) sandy clays (essentially quartz—montmorillonite—hydromica clays; 2) carbonate—clayey (hydromicaceous), essentially quartz sandstones; 3) clayey quartzites; 4) clayey—carbonate sandstones (clayey—calcite—quartz sandstone). In brackets — number of samples.

pure varieties (CaO 44.83-55.09%; MgO 0.43-7.38%; CO₂ 41.9-43.30%); but arenaceous varieties (SiO₂ 16.58-34.03%) do occur.

Investigations of carbonate rocks of the complex indicate that these rocks are "impoverished" with respect to Cr, Ni, V, Pb, Y, B, and a number of other microelements relative to clarkes for carbonate deposits of the Phanerozoic. The concentrations of Sr found in the deposits studied are quite interesting; this element is characteristic of carbonates, in which it geochemically binds to Ca. In the investigated carbonate rocks of the Riphean, the greatest concentrations of Sr (up to 3000-3600 g/ton, an average of 1929 g/ton based upon 10 samples) are restricted to limestone, whereas dolomite is "impoverished" with respect to this element (Sr = 60-130 g/ton). The same pattern is typical of Ba (30-90 g/ton in limestone; < 30 g/ton in dolomite). Formation of carbonate deposits R₁₋₂ probably took place in a shallow-water paleobasin. Evidence in favor of such an origin includes the small thicknesses of packets (of dolomite and limestone) in these rocks as well as the presence of sandy and gravelly varieties, coupled with an almost complete absence of clayey varieties. In this case, sedimentation probably took place under shallow-water conditions, since, according to data presented in [5], dolomite deposits concentrate toward nearshore zones of paleobasins and stromatolithic bioherms are typical of precisely such shallow-water (sublittoral) environments. It is possible that the water of this paleobasin was of elevated salinity; high concentrations of Sr in limestones, high Sr/Ba values, and the presence of dolomite in the sections are evidence in favor of this.

The limestone is overlain by a carbonaceous rock sequence (2.5-3.0 km) which, according to data presented in [10], can be assigned to the "Black Schist" Formation. Most rocks of this sequence are grey or dark grey as a result of substantial content of carbonaceous material. Schists principally consists of sericite, chlorite, and carbonate with a substantial admixture of finely dispersed carbonaceous material. Pyrite occurs fairly frequently in the schists. Among the sequence of phyllitic schists, there are thick (1-3 m) interbeds of quartzite and carbonate-containing schist. The regional metamorphism of the rock corresponds to the greenschist facies. In terms of chemical composition, primarily SiO₂ and Al₂O₃ content, the rocks of the

TABLE 3. Abundances of Microelements in Pyrites, g/ton

Sample number	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo
1/15	25	111	59	200	63	37	<10	3,2	11,8
1/36	125	32	160	120	28	22	<10	~1,5	20,0
1/42	14	51	20	310	127	35	<10	~1,5	14,8
1/43	54	86	62	105	142	12	<10	<1,5	9,5

Explanation. The analyses were performed in the analytical-chemical laboratory of the Institute of Geology, Russian Academy of Sciences (I. Yu. Lubchenko, analyst).

TABLE 4. Abundances of Microelements in Carbonaceous Deposits, g/ton

Sample number	Cr	V	Ni	Co	Cu	Nb	Sc	Mo	Y	Yb	B	Sr	Zr	Ti
1/15	10	15	7	1	1	10	8	8	40	3	0,5	<100	~1	0,08
1/19a	—	—	2	1	2	2	1	8	25	4	0,01	<100	~1	0,001
1/20b	—	8	1	2	3	70	1	4	1000	22	0,4	100	~1	0,85
1/22	50	140	40	2	15	100	10	—	600	20	>1	350	0,17	>1

Explanation. Abundances of B, Zr, and Ti are given as percentages. The analyses were carried out at the spectral laboratory of the Institute of Geological Sciences of the Ukrainian Academy of Sciences (N. P. Verkholyad, analytical chemist).

sequence can be subdivided into four groups: aluminiferous shales, quartz-mica schist, carbonate-containing schist, and quartzite (Table 1). It should be noted that aluminiferous shales show the greatest contents of C_{org} . These values are typical of clay shales of the Phanerozoic, but quartzites and carbonate-containing schists also contain substantial quantities of carbonaceous material (see Table 1).

We attempted to reconstruct the quantity of C_{org} (OM) present in the original deposits. Thus, according to the data of a number of investigators (N. M. Strakhov, V. N. Kholodov, O. V. Bordovskiy), from 23 to 43% of sedimentogenic OM is lost during diagenesis. For our calculations, we will assume an average loss of 35% of OM during diagenesis, with 75% of the OM lost during the catagenesis accompanying diagenesis. Using these losses (35 and 70%) and assuming a conversion factor of C_{org} to OM equal to 1.43, we find that there probably was an average of 5.6-7% C_{org} (8-10% OM) initially present in aluminous deposits, 2-4% C_{org} (3-5.5% OM) initially present in sandy and clayey-sandy deposits, and 3.5-4.2% C_{org} (5-6%) initially present in carbonate deposits. Thus, the content of C_{org} in the parent rocks of the "Black Schist" Formation of the Riphean substantially exceeds the C_{org} content in otherwise similar rocks of the Phanerozoic. According to Ronov's data [15], the content of C_{org} in ranges from 0.52 to 1.14% clays and clayey shales, from 0.20 to 0.37% in sands and sandstones, and from 0.22 to 0.45% in carbonate deposits in various structural zones of the Phanerozoic.

As is well known, the composition of sandy-clayey rock depends upon the type of geotectonic structures the rocks are formed within. Thus, the rocks of the Ul'dzit-Golsk complex investigated, based upon the pattern of points plotted on a Mishkin diagram [11], can be classified as sandy and clayey shales of miogeosynclines and platforms. Ratios of alkaline and alkaline-rare-earth elements suggest that the deposits investigated are of the potassic-magnesian type; values of $FeO_{tot}/CaO+MgO > 1$ from the rocks investigated indicate that they are rocks of high iron content. On a Neyelov diagram [12], points plotted for rocks of the "Black Schist" Formation form a trend extending from the field of quartz sandstones to the field of clays from hot, humid climates. Based upon values of Al_2O_3/SiO_2 values (0.03-0.49), the rocks investigated correspond to the series quartz sandstone (arenite) (0.03)-clay (0.37)-clay of hot, humid climates (0.56). Middleton's coefficient ($Na_2O + K_2O/Al_2O_3 = 0.22-0.26$) suggests that the potassium in the rock is bound to clay material. Values of K_2O/Al_2O_3 (0.02-0.29), K_2O/MgO (0.30-5.81) and Σ alkaline + alkaline-rare-earth elements/ Al_2O_3 (0.32-0.90) indicates transition the clays are probably a mixture of hydromica, montmorillonite, and kaolinite. Use of a methodology [14] for lithochemical conversions of Riphean rocks investigated to normative-mineral compositions of parental deposits (Table 2) also suggests that clay minerals, primarily hydromica, composed a substantial portion of the original sediments. Montmorillonite was present in substantial quantities in the parental deposits of aluminiferous shales. Kaolinite and chlorite were consistently

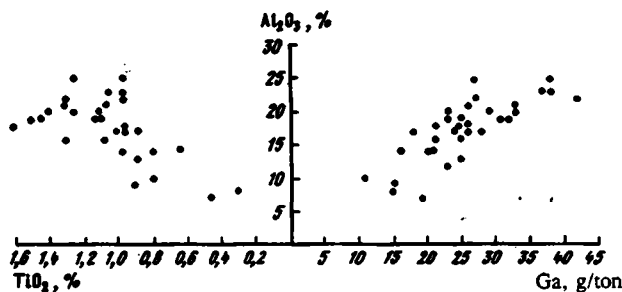


Fig. 1. Dependence of TiO_2 and Ga upon Al_2O_3 content in rocks of the Ul'dzit-Gol' complex.

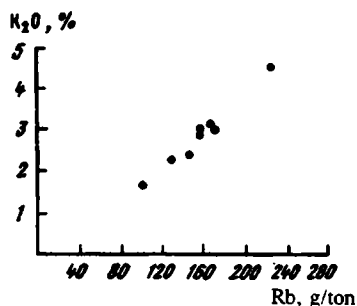


Fig. 2

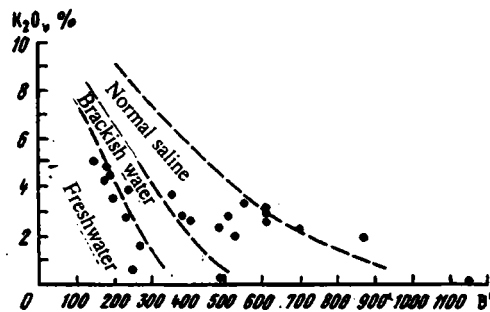


Fig. 3

Fig. 2. Relationship between Rb and content of K_2O in rocks of the Ul'dzit-Gol' complex.

Fig. 3. Points for rocks of the Ul'dzit-Gol' complex plotted on a K_2O -B' diagram.

present in smaller quantities; perhaps appreciable quantities of these minerals (1-3%) as well as serpentine should be considered consequences of elevated (in comparison to values used in the formula) contents of Mg and Al in modal hydromica. The clastic fraction of the parental deposits primarily consisted of quartz. The ratio of normative feldspars indicates substantial predominance of plagioclase (primarily acidic—albite) with a quite negligible role for K-feldspar. This is probably a result of a deficit of the latter in the rocks of the source area. The carbonate component of the sandy-clayey parental deposits was quite minor; it reached substantial amounts only in the original material of the carbonate-bearing schists (see Table 2). The parental deposits of the "Black Schist" Formation had somewhat elevated iron content (the iron index ranges from 0.68 for aluminiferous shales to 0.77 for mica-quartz schists).

Metavolcanite bodies are fairly common within the "Black Schist" Formation. However, the average values of Strakhov's modulus ($\text{Fe} + \text{Mn}/\text{Ti}$), which do not exceed lithogenic values $(10-20) \pm 5$ suggest that postvolcanic gas-hydrothermal activity may have had almost no influence on the formation of the sediments.

A characteristic feature of rocks of the "Black Schist" Formation is the presence of pyrite mineralization. Pyrite is represented by well formed crystals (up to 0.5-1 cm) which are typically covered at the top by brownish-rust colored oxides. An analysis of monofractions of these pyrites revealed that they contain substantial quantities of Ni (averaging 70 g/ton), Cu (averaging 184 g/ton), and Co (averaging 90 g/ton). However, some weathering of pyrite probably resulted in reductions in the concentrations of a number of microelements within it, such as Pb and Mo (see Table 3). For example, the average content of Pb equals 307 g/ton in pyrites of sediments in the Black Sea, but reaches 200-500 g/ton in pyrites of Paleozoic black shales of Pay-Khoya and the northern Urals [3, 9]. Interestingly, vanadium is consistently present in all of the sulfides (20-160 g/ton, averaging 75 g/ton); to some degree, this suggests a primary-sedimentary origin for the pyrites examined.

In addition, we analyzed monofractions of carbonaceous material (Table 4). The data presented shows that carbonaceous material of Riphean rocks is distinctly "impoverished" with respect to a number of biophilic elements, including V, Ni, Co, Cu, and Mo relative to both pyrites (see Table 3) and the enclosing rock (Table 5). At the same time, this material contains substantial quantities of B, Zr, and Ti (see Table 4), which (Zr, Ti) are not typical biophilic elements. A substantial portion of microelements (Pb, Zn, Ag, Bi, Sb, Hf, Co, Ta, W, Ba, Ga, Ge) in the samples examined are not very common.

TABLE 5. Average Concentrations (in numerator) and Ranges of Variation (in denominator) of Minor Elements in Rocks of the Ul'dzit–Gol' Complex, g/ton

Rock	Cr	V	Ni	Co	Cu	Pb	Ga	Ge	Mo	B	Ba	Sr	Ti	Fe _{tot}
Aluminiferous shales (16)	$\frac{91-700}{181}$	$\frac{115-600}{237,5}$	$\frac{30-112}{55}$	$\frac{6-24}{13,5}$	$\frac{17-87}{41}$	$\frac{10-28}{16}$	$\frac{23-42}{31}$	$\frac{1,8-1,3}{2,6}$	$\frac{1,5-3,7}{2,5}$	$\frac{79-230}{153(9)}$	$\frac{340-900}{558(9)}$	$\frac{90-500}{223}$	$\frac{0,57-0,90}{0,7134}$	$\frac{2,74-6,95}{5,15}$
Quartz-mica schists (13)	$\frac{68-270}{126}$	$\frac{93-475}{217,8}$	$\frac{17-100}{38,4}$	$\frac{5-20}{9,9}$	$\frac{15-135}{41,8}$	$\frac{10-41}{16,8}$	$\frac{16-28}{22,9}$	$\frac{2,3-3,6}{2,8}$	$\frac{1,5-5,3}{2,28}$	$\frac{75-210}{119,2}$	$\frac{290-950}{560}$	$\frac{50-250}{124,6}$	$\frac{0,38-1,10}{0,7014}$	$\frac{2,64-16,03}{5,34}$
Quartzites (7)	$\frac{30-323}{142}$	$\frac{50-245}{129}$	$\frac{17-68}{43}$	$\frac{5-20}{10}$	$\frac{15-110}{49}$	$\frac{5-24}{12}$	$\frac{<10-25}{<10-25}$	$\frac{1,5-5,7}{2,3}$	$\frac{1,5-7,0}{4,1}$	$\frac{20-200}{73(5)}$	$\frac{60-300}{148(5)}$	$\frac{30-140}{72}$	$\frac{0,18-0,55}{0,3117}$	$\frac{1,08-5,86}{3,49}$
Carbonate-containing schists (3)	$\frac{21-130}{84,3}$	$\frac{21-235}{130,3}$	$\frac{21-88}{53,3}$	$\frac{6-42}{21,3}$	$\frac{16-69}{35}$	$\frac{10-20}{14}$	$\frac{<10-21}{<10-21}$	$\frac{<1,5-3,2}{<1,5-3,2}$	$\frac{1,8-5,7}{3,2}$	$\frac{100(1)}{100(1)}$	$\frac{280(1)}{280(1)}$	$\frac{90-470}{246,6}$	$\frac{0,22-0,61}{0,3657}$	$\frac{3,07-4,80}{3,99}$
Schists	90	130	68	19	45	20	19	1,6	2,6	100	580	300	0,46	4,72
Sandstones	35	20	2	0,3		7	12	0,8	0,2	35		20	0,15	0,98

Explanation. Number of samples analyzed is given in brackets. Concentrations of Ti and Fe_{tot} are given as percentages. In seven samples of aluminiferous shales, we found, in g/ton: Nb 14-20 (average of 19.1); Zn 50-140 (average of 104); Rb 129-227 (average of 166); Y 21-71 (average of 41); Zr 186-270 (average of 224). Concentrations of minor elements in Phanerozoic schists and sandstones are taken from [18]. Analyses were performed in the chemical–analytical laboratory of the Institute of Geology, Russian Academy of Sciences (A. I. Gusareva and N. A. Solenkova, analytical chemists).

A substantial number of microelements are not regularly detected; this can probably be explained by removal of a substantial portion of microelements from carbonaceous material during separation of such material by means of acids.

Abundances of microelements in sample of the "Black Schist" Formation varied widely (see Table 5), but a substantial number of microelements were consistently present in elevated quantities relative to clarkes for sedimentary deposits. Thus, the elements Cr, V, Ti, Ga, B, and Fe are present in elevated quantities in all of the rock types investigated (see Table 5), with maximum concentrations of the majority of these elements restricted to aluminiferous varieties. It should be noted that correlations of Ti and Ga with Al_2O_3 (Fig. 1) and Rb with K_2O (Fig. 2) are clearly evident in the samples investigated. Quartzites of the Ul'dzit-Gol' complex contain, in addition, quantities of Ni, Co, Pb, Ge, Mo, and Sr which are higher than clarkes for sandstones (see Table 5). The elevated contents of these elements can probably be explained by the fact that the quartzites contain substantial quantities of argillaceous and organic material, which are concentrators of a number of microelements, and the fact that Ge is frequently concentrated in silicates as a result of the crystal-chemical similarity between Ge and Si (see Tables 1 and 2).

Concentrations of a number of indicator elements (Cr, Ti, Fe, V, and others) and values of $\text{TiO}_2/\text{Al}_2\text{O}_3$ ranging from 0.057 to 0.086 (>0.05 in basic rocks and <0.03 in granitoids) probably means that the rocks of the source area primarily were rocks of basic composition and, to a lesser degree, rocks of ultrabasic (Cr up to 700 g/ton) and acidic (Zr up to 270 g/ton, Rb up to 227 g/ton) compositions.

The good correlations of Ti and Ga with Al_2O_3 (see Fig. 1) and of Rb with K_2O (see Fig. 2), as well as values of $\text{Al}_2\text{O}_3/\text{TiO}_2$ ranging from 11.62 to 17.66, may indicate a supply of well differentiated material to the sedimentary paleobasin and a paleoclimate of the humid type.

As is well known, the most reliable indicators of water salinity in paleobasins are B and Ga, which are present primarily (with the exception of tourmaline and other accessory minerals) in the clay fractions of sediments. Ga is associated with continental deposits and B is associated with marine deposits. The substantial amounts of B in the rocks (see Table 5) probably indicate a marine origin, since freshwater deposits contain B in amounts of 44-54 g/ton, whereas marine deposits can contain B in quantities of 100-110 g/ton [6]. On a B-Ga diagram, most points plotted for rocks of the "Black Schist" Formation lie within the field of marine shales. Although it is true that points are more uniformly distributed on a $\text{K}_2\text{O}-\text{B}'$ diagram (where $\text{B}' = \text{B} \cdot 8.5/\text{K}_2\text{O}$) (Fig. 3), points representing mean values (for 25 samples, with the highest and lowest values discarded) lie within the field representing rocks formed in a paleobasin with normal mineralization of water. A quantitative determination of the paleosalinity of a sedimentation basin based upon the formula $S = (\text{B}/27.9)^{2.32}$ [17] yielded a value (31‰) corresponding to a normal saline composition for water in a marine basin.

Thus, the evidence of life activity of very simple organisms (stromatolites, oncolites), organic remains, and substantial quantities of carbonaceous material suggest flourishing life in a Riphean paleobasin. Carbonate sediments were probably deposited in a shallow-water paleobasin with elevated salinity. During sedimentogenesis of the deposits forming the "Black Schist" Formation, the paleobasin probably contained deeper water (100-200 m) of a typical marine composition, although reducing conditions with traces of hydrogen sulfide pollution probably existed in the near-bottom part of the paleobasin.

Rocks of the Ul'dzit-Gol' complex, which are special for their contents of a number of ore elements (Cr, V, Ti, Ge, etc.), were probably a source of ore matter during subsequent metasomatic-metamorphic conversions. The region is still considered promising for gold mineralization [7, 8, etc.] associated with rocks of the "Black Schist" formation.

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THE ORIGIN OF THE PARAGENESIS OF NONFERROUS METALS AND NAPHTIDES IN CARBONATE-TYPE SEDIMENTARY BASINS

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In this article, we present evidence for a paragenesis of stratiform lead–zinc deposits localized in carbonate rocks and naphthide in sedimentary basins of the carbonate type. We suggest that the cause of this paragenesis is the similar behaviors of lead, zinc, and organic matter during sedimentary–diagenetic and catagenetic stages in the transformation of argillaceous and carbonate rocks of sedimentary basins.

The problem of paragenesis of ore and naphthide deposits can be solved with the aid of data from lithology and paleohydrogeology together with investigations into the formation of oil, gas, bitumen, and ore deposits. Unfortunately, most of these studies are being conducted in isolation from one another; this is especially true of investigations of ore and oil–bitumen deposits.

The possibility of a connection between ore formation and oil formation was first suggested by V. I. Vernadskiy at the beginning of the twentieth century. In 1926, E. A. Bastin (USA) pointed out that lead–zinc deposits of North America, subsequently classified as belonging to the Mississippi type, are associated with heavy oil and bitumen. The reports of American researchers (B. Doy, E. Noble, A. Heyl, J. Anderson, R. Macqueen, G. Gerven, Z. Dozy, D. Sverzhenskiy, etc.) and Soviet researchers (A. S. Uklonskiy, A. I. Germanov, G. L. Pospelov, V. V. Popov, V. N. Kholodov, B. A. Klubov, N. S. Beskrovnyy, I. G. Gol'dberg, etc.) have shed light on this problem.

Here, we will consider this question as it pertains to stratiform lead–zinc deposits. Evidence suggesting a paragenesis of ore deposits of these types and naphthides has been presented in many reports [4, 6, 8, 13, 14, 17–20, 22, 23]. In the case of stratiform lead–zinc deposits, this evidence can be summarized as follows:

- 1) confinement of these deposits and naphthide deposits to long-existing and steadily developing positive local structures complicating the overall subsidence of oil-and-gas basins. Often, these positive structures can be identified by carbonate deposits and reef structures, which occasionally play a direct role in localizing lead-zinc and oil-and-gas deposits (Figs. 1 and 2);
- 2) control of lead–zinc and naphthide deposits by shared, long-existing faults along which ore-bearing and gas-and-oil-bearing fluids have moved (Fig. 3);
- 3) similar temperatures of formation (50–200° C) of lead-zinc ores and oil-and-gas occurrences in the principal zone of oil and gas formation;
- 4) close spatial association of naphthides and lead-zinc ores with evaporites;
- 5) widespread distribution of neogenic minerals in oil and gas reservoir rocks; these minerals are similar to minerals composing stratiform lead–zinc ore bodies (pyrite, sphalerite, galena, quartz, dolomite, calcite, barite, fluorite, etc.);
- 6) elevated concentrations of organic matter in host rocks in comparison with underlying and overlying rocks;
- 7) the presence of bitumen and hydrocarbon gases in gas-liquid inclusions in minerals found in the ores of lead–zinc deposits;
- 8) content of ore components of lead, copper, and especially zinc in oil. The content of zinc in a colloidal solution of oil can reach 8% [3].

We believe that the enumerated facts indicate similar conditions of formation of stratiform lead–zinc deposits and naphthides at various stages in their creation and that it is therefore useful to discuss such similarities, starting with the stage of sedimentogenesis and ending with the stage of subsequent transformation of ore and naphthide parageneses.

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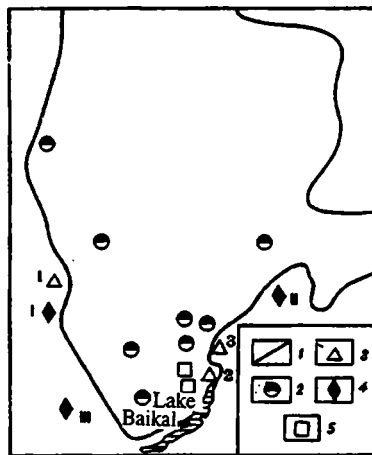


Fig. 1

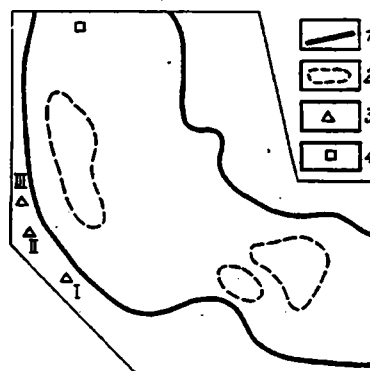


Fig. 3

Fig. 1. Map showing locations of oil-and-gas deposits of the Lena-Tunguska province and ore deposits. 1) boundary of the Lena-Tunguska oil-and-gas province; 2) oil and gas fields in Riphean and Vendian deposits; 3) stratiform lead-zinc deposits of Riphean and Vendian age (1: Gorevsk; 2: Tabornoye; 3) Barvinskovo); 4) gold-sulfide deposits of Proterozoic age (I: Olimpiadninsk; II: Sukhoy Log; III: Zun-Kholbinsk); 5) ore show of cupriferous sandstones.

Fig. 2. Map showing oil-and-gas geological regionation of the Chu-Sarysuisk province and the locations of ore deposits. 1) boundaries of the Chu-Sarysuisk gas region; 2) boundaries of gas regions with fields coinciding with Famennian deposits; 3) stratiform lead-zinc deposits (I: Mirgalimsay; II: Talap; III: Shalkiya); 4) Dzhezkazgansk deposits of cupriferous sandstones.

The entire process of formation of sulfide deposits associated with oil and gas shows can be divided into two main stages: sedimentary-diagenetic and catagenetic.

THE SEDIMENTARY-DIAGENETIC STAGE

Processes involved in the formation of concentrations of organic matter and metals (in particular, lead and zinc) begin with sedimentation of argillaceous and carbonate rocks rich in organic matter. According to various investigators, the abundance of OM in the Earth's crust varies over a wide range. Clarks of OM in different rocks equal, in %: 0.2 in carbonate; 0.2 in arenaceous; 0.45 in aleuropelitic; 0.9 in argillaceous rocks.

The chief source of carbonaceous material of biogenic origin is remains of dead organisms: autochthonous detritus and allochthonous fossils of continental origin forming accumulations in the near-bottom part of the ocean, and, especially, water-soluble forms of organic matter, primarily represented by organic acids, liquid and gaseous hydrocarbons, nitrogen compounds, etc.

Most of the organic matter is deposited in associated with clays at passive submarine margins of continents. As corrected pointed out in [7], such an area is, from a hydrodynamic and hydrochemical point of view, a zone of mixing of nearshore fresh water rich in oxygen and mineralized ocean water; it can also be considered a zone of mixing of slightly acidic continental water rich in humic acids and slightly alkaline ocean water. Experimental data indicates that lead and zinc in the form of carbonate and hydrosulfide complexes are highly mobile; this can be explained by the presence of organic acids. Precipitation of these metals in the sulfide form takes place only in an environment of low pH during coagulation of organic acids in a zone where marine and continental waters mix. Therefore, this zone is a unique geochemical barrier where coagulation of organic acids and precipitation of sulfides take place.

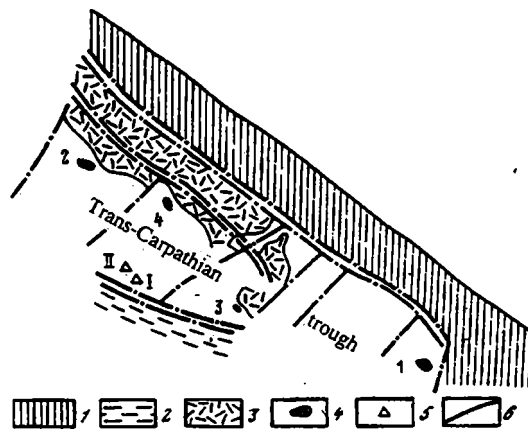


Fig. 3. Shape showing locations of gas, gold-polymetallic, and lead-zinc deposits of Trans-Carpathia. 1) Fold zone of the Carpathians; 2) Pannonian massif; 3) Vagorlat-Gutinsk volcanic ridge; 4) gas deposits (1: Soltvinsk; 2) Russko-Komarovsk; 3) Korolevsk; 4) Stanovsk); 5) ore deposits (I: Beregovsk gold-polymetallic; II: Began'sk lead-zinc); 6) faults.

Bacteria play an important role in sedimentogenesis. Their activity has a bearing upon whether an oxidizing or reducing environment is created and controls the gas regimes of the zones mentioned. Dying organic matter generates CO_2 , N_2 , and NH_3 under the influence of bacteria in an oxidizing environment and generates CH_4 , CO_2 , H_2S , H , and hydrocarbons in a reducing environment. Organic matter plays the role of a feeding environment for bacteria; many investigations have shown that both methane-naphthene and aromatic hydrocarbons can serve as food for bacteria. The life activity of anaerobic bacteria generates H_2S , causing precipitation of sulfides.

As already noted, clays are the main facial type of rock deposited at passive continental margins. The highest clark concentrations of nonferrous metals are found precisely in such environments. Thus, according to the data of I. Yu. Lubchenko, the average content of lead is $7 \cdot 10^{-4}\%$ in sandstones of recent marine sediments, $9 \cdot 10^{-4}\%$ in carbonate rocks, and an order of magnitude higher, $80 \cdot 10^{-4}\%$, in clays. As N. M. Strakhov pointed out, combinations of such deposits form for the most part in arid climates and, consequently, such parageneses of rocks typically include evaporites, predominantly of sulfide composition; evaporites typically playing a role in the compositions of metalliferous sections. As pointed out by V. M. Popov and U. Asanaliyev, potentially ore-enclosing horizons of carbonate rock accumulate during periods of maximum transgression, whereas evaporites primarily accumulate during regressive stages in the evolution of structures. Therefore, these formation usually occupy different stratigraphic positions, evaporates frequently lying above carbonate deposits.

Carbonate formations, which primarily consist of limestones and dolomites alternating with layers of conglomerates aleulites and clayey shales, are among the most important geological formations containing organic material. Rocks of such formations are characteristic of margins of platforms and median masses, where they are occur in epicontinental basins on continental-type crust. Lead-zinc and naphthide deposits are frequently associated with such formations.

THE CATAGENETIC STAGE

The second stage in the geological history of organic matter and nonferrous metals is associated with processes of cata- and metagenesis of sediments at passive zones of continents. During this period, sequences of clay rock are covered by younger sediments and subjected to epigenetic alterations under the influence of elevated temperature and pressure, primarily consisting of dehydration of clays. The second stage in dehydration of clays, discussed in detail by M. Powers and J. Berst, is of special importance. Their ideas are based upon the view that there are swelling (montmorillonite and montmorillonitic mixed-layer minerals) and nonswelling (hydromica, chlorite, and kaolinite) components in marine clay sequences and that swelling minerals are transformed into nonswelling minerals, accompanied by separation of water, during catagenesis and

burial of the sediments [6, 16]. The water released probably redistributed disseminated components of the enclosing rock, including lead, zinc, and copper.

Organic matter undergoes substantial alterations during diagenesis and catagenesis; during this process, leaching of low-temperature-cracking products and release of gas ($\text{CH}_4 - \text{C}_8$) and bituminoids take place. Intramolecular grouping of atoms and polymerization occurs in the kerogen itself and asphalts are thus converted into asphalts and kerites. In the process, there are increases in the contents of humic and fulvic acids and humins, as well as acetate, axolate, and succinate complexes, which play an important role as transport agents for ore elements in the form of complex metallo-organic compounds [8, 24]. The investigations of E. Degens demonstrated the presence amino acids in stratal waters of petroliferous regions and carbonic acids (up to 3 mg/liter) in deep pressure waters of oil-and-gas fields.

Elevated temperatures under conditions of mesogenesis and catagenesis (the main stage of oil formation, according to N. B. Vassoyevich) result in enrichment of aqueous solutions with hydrocarbons, intensive formation of mobile hydrocarbon compounds, and concentration of microelements. In the opinion of Ermolayev and Sozinov [7], catagenesis results in migration of ore components captured by organic matter during sedimentogenesis; during this process, structural alterations of organic matter of the sapropelic type are accompanied by a change of ore cation together with incorporation of a highly mobile metal into the interior of the kerogen molecule. In the case of organic matter of humic origin, an increase in catagenetic coalification is accompanied by displacement of microimpurities toward to periphery of the molecule; this makes possible movement of microimpurities into filtering solutions and leaching of such impurities from the rock. In this connection, according to the data of Ermolayev and Sozinov, sediments with humic organic matter show a tendency toward dissemination of ore elements, even at the stage of catagenesis, whereas sediments with sapropelic organic matter retain their metals right up to the point of regional metamorphism.

Investigations by Ilyaletdinov [6] show that biological immobilization of metals can take place by absorption of metals by plants, microorganisms, and raw organic matter. Accumulation of copper, lead, and zinc in plant cells occurs in reeds, rushes, cattails, sedges, and other plants. Many animals organisms also possess this property. Thus, concentrations of these metals are higher, in the soft tissues and skeletal parts of present-day coral polyps, molluscs, and medusas than in the surrounding environment: 2600 times higher in the case of lead and 3200 times higher in the case of zinc [21]. Bacterial biomass contains the following concentrations (in mg per 100 g dry weight): Cu 12; Zn 0.1-28; Pb 0.6-1.5; Ba 18-50. According to the data of Ilyaletdinov, humic acids and fulvic acids accumulating during the initial stages in the transformation of humic acids play an important role in the binding of metals and organic matter. Copper in ionic form binds primarily with humic acids (93%); lead binds primarily with fulvic acids (92%); zinc is found to equal extents in both types of acids [6]. As a result of reactions of metals with products of microbial breakdown of organic compounds, relatively stable, poorly mobile metalloorganic compounds are formed.

Many investigators [1, 5, etc.] have turned their attention to the coincidence of stratiform lead-zinc deposits with the peripheries of saline basins. As shown in [1, 25], interaction of groundwaters with evaporites causes increased salinity and increased dissolving power of aqueous solutions. Their capacity to leach metals, including lead and zinc, sharply increases in the the process. According to the data of E. A. Baskov, chloride brines with high metal contents form in the zone of catagenesis of carbonate-terrigenous rock as these rocks interact with halogene formations. Such brines can show the following concentrations of metals (in mg/kg): Zn up to 10-100; Pb up to 5-10; Cu 0.5-5; Ag up to 0.4-24. The temperatures of such brines can reach 250°C or more at depths of 3-5 km.

The brines created are initially rich in magnesium and are subsequently altered according to the following pattern: $\text{Cl-Mg-Na} \rightarrow \text{Cl-Mg-Ca} \rightarrow \text{Cl-Ca-Mg} \rightarrow \text{Cl-Ca}$ [10]. The presence of gypsum and anhydrite crystals in the interstices of suggests an influence of halogene sulfate brines upon calcium-containing rocks via a reaction of the type: $\text{MgCl}_2 (\text{solution}) + \text{Ca} (\text{rock}) = \text{CaCl}_2 (\text{solution}) + \text{Mg} (\text{rock})$ or $\text{MgSO}_4 (\text{solution}) + \text{Ca} (\text{rock}) = \text{CaSO}_4 + \text{Mg} (\text{rock})$.

In stratiform lead-zinc deposits, these processes are expressed mineralogically as epigenetic dolomitization of limestones preceding precipitation of lead and zinc sulfides. In the opinion of Krainov et al. [10], estimates of energy advantage and experimental investigations support the hypothesis that dolomitization is the process which replaces calcium in carbonate rocks.

Forms of transport of metals (including lead and zinc) into brines have been insufficiently studied. As noted by R. G. Rafal'skii, chlorides are the main form of transport of these and many other metals. Moreover, according to the data of L. S. Fafel', amino acids, as well as fulvic, humic, and carbonic acids have the ability to form complexes in an alkaline medium with enrichment of rocks and water with organic matter. In such an environment, transport of lead and zinc in the form of easily dissolved metallo-organic complexes can take place. This leads to precipitation of the metals in the form of poorly

soluble metallo-organic compounds or, if the concentration of H_2S is sufficient, precipitation in the form of sulfides. Thus, the presence of dehydrated water, humic acids, fulvic acids, acetate compounds, the formation of metamorphic compounds, and the existence of common migration pathways of organic matter, lead, and zinc, as well as the creation of brine waters, probably indicates similar geochemical fates of naphthides, lead, and zinc during the stage of catagenetic transformation. One should note, however, the isolation of these deposits in local plan. Oil and gas pools form major portions of central areas of oil-and-gas basins in porous and fractured rocks, sandstones and limestones typically referred to as fluid conduits or reservoirs. Evaporites represented by salt beds or clays and clayey shales primarily serve as barriers. Barrier rocks typically lie above reservoir beds (superstratum), but occasionally lie below them (substratum). Fluid conduits often pinch out along strike and are replaced by rocks unfavorable for formation of oil and gas pools.

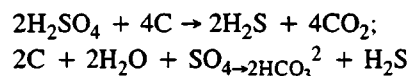
As for lead-zinc ores, ore-bearing solutions containing these metals are transported along porous beds-conduits and faults to areas of lower lithostatic pressure, where magnesium contained in the solutions can start to interact with limestone, forming metasomatic dolomite. Formation of lead and zinc sulfides from these solutions takes place at the sulfide barrier, which is formed by water containing reduced sulfur in the rock [11].

During breakdown of oil and gas accumulations, a process already underway as oil-and-gas pools form, organic matter is transported in an upward direction, i.e., directly upward through the roof along faults or in a lateral-ascending direction along bed rise.

Klubov [9] as well as Germanov and Chinenov [2] concluded that ancient deposits of oil or naphthide bitumens subjected to destructive processes were the source of bitumens associated with ores. As is well known, accumulations of bitumens can form in a zone of hypergenesis as a result of two stages in oil migration, an accumulation stage and a dissipation stage [6]. Such deposits are localized primarily at the peripheries of oil-and-gas basins, where bitumens migrate after destruction of oil and gas deposits. These areas are also favorable for localization of stratiform lead-zinc deposits, since they coincide with areas when metalliferous petroliferous brines are discharged.

One cause of the association of bitumens with sulfide ores is the activity of sulfate-reducing bacteria, which use bitumens has a feeding environment. Sulfate-reducing bacteria are viable over a pH range of 4.2-10 and an Eh range of +110 to -500 mV under quite diverse temperature conditions.

The prevalent impression that such bacteria are viable only under low-temperature conditions now must be reconsidered in view of the recent discovery of similar bacteria in present-day sulfide formations of ocean floor formed at temperatures of 300-350°C (ore shows on mid-ocean ridges as well as the gulfs of California and the Mississippi) [12, 13]. Sulfate-reducing bacteria are found most frequently in magnesium-rich solutions; their numbers depends upon the content of organic matter which can be broken down as a source of energy. In a reducing environments found in bottom sediments, the concentration of sulfate-reducing bacteria is typically 10^3 - 10^5 per 1 g of sediment. Formation of reduced sulfur and precipitation of sulfides of lead, zinc, and copper have been demonstrated in experiments by Kramarenko [12], which yielded galena, covellite, greenockite, and chalcopyrite, whereas sulfide formation has not been detected in experiments without the use of bacteria. The chemical essence of the bacterial process is reduction of sulfates in sea water and formation of hydrogen sulfide. This can be schematically represented by the following biochemical reactions:



In summary, it should be noted that the paragenesis of deposits of non-ferrous metals and oil-and-gas shows is due to genetic factors, namely, similar depositional environments of organic matter and metals in sedimentary basins, similar behavior during catagenesis, and also common patterns of formation of bitumens and shows of nonferrous metal sulfides.

As is well known, there are various points of view concerning the origin of the carbonaceous material. According to one theory, developed by the authors of the present article, the carbonaceous material is of organic origin and is a result of sedimentation and catagenesis of sedimentary rock; according to another theory, the carbonaceous material is of nonorganic origin and is a product supplied from layers of the mantle.

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UPPER PROTEROZOIC GEOLOGY AND HYDROCARBON PROSPECTS, METROPOLITAN MOSCOW DISTRICT*

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New data on the geological makeup of the Teplostansk Graben of the Moscow Aulacogen deals with lithological-geochemical rock characteristics in deep drillholes in the Moscow area and about the enclosed bituminoids. Hydrocarbon prospects of the Upper Proterozoic beds in the graben have been evaluated.

Upper Proterozoic deposits of the East European Platform have long been of interest, primarily in evaluating hydrocarbon prospects. This topic was discussed in a number of papers [1, 4, 6, 8, 10, et al.]. Hydrocarbons have been produced in the eastern Russian Plate from Vendian deposits. The Vendian deposits were found in the Permian Pre-Ural region (Sivensk, Larionovsk, etc.) and the Orenburg District (Okruzhnoe). Hydrocarbon shows occur at a few locations and are associated with Riphean deposits [9]. In the Soligalich Aulacogen only noncommercial oil shows occur in the Danilovsk area Vendian beds with high electric resistance values. Deep drillhole data (1991-1992) from the Moscow area are of interest. They supplement current assumptions on the geological composition and hydrocarbon content of old stratigraphic units in the central Russian Platform area.

One of the largest negative structures of the southwest Moscow Syncline occurs in the east-west oriented Moscow Aulacogen. It is approximately 450 km long and maximum 40 km wide. The Teplostansk Graben is one of the deepest buried structural elements in the aulacogen. The crystalline basement at Novye Cheremyushki Subway Station is 2.8 km deep. On the north and south the graben is bounded by the Lyuberetsk, respectively, Zvenigorod horst ridges. The basement is 1.6-2.0 km deep here. North of the graben, the Krasnogorsk Ridge is combined with the Istrinsk-Kol'chuginsk Ridge, the highest horst ridge that was uplifted 1.4 km above the buried basement surface in the Strogino area. The Tumsk-Shatursk Ridge is located south of the graben. The area of the Teplostansk Graben is 600 km².

In the grabens, the Proterozoic sediment surface slopes westward, toward the Pavlovo-Posatsk fault zone at a rate of maximum 20 m/km. Two elongated, uplifted ridges along the flanks of the graben rise from the Riphean sediment surface. They are oriented in east-west direction. The Moskvoretsk Ridge occurs on the north, the Vidnovskii Ridge on the south. The better studied Moskvoretsk Ridge runs along the fault. It is 35 km long 3-4 km wide and displays a steep slope, inclined at maximum 3 degrees. The flat southern limb has an amplitude of 30-40 m. Upward, in the section, the ridge become smaller and at the level of Mesozoic deposits does not exceed 2 km × 10 km.

In the Moscow Aulacogen the basement is composed of various Archean-Proterozoic metamorphic and igneous rocks. Drillholes P-5 and P-7 penetrated the basement only in the Krasnogorsk Horst between 1576-1578 m. Crystalline basement in drillhole P-7 contains plagioclase-pyroxene, biotite-pyroxene-plagioclase and garnet-pyroxene-plagioclase granulites of granoblastic and porphyroblastic texture. The first granulite variety contains minor amounts of small dolomite and magnetite grains. The rock density equals or exceeds 3 g/cm³. In granulite found 10 m below the basement surface, the C-isotope content in dolomites equaled +7.6‰; in the organic matter, -24.9‰. The crystalline basement rocks in drillholes

*The presented interpretations are based on conclusions obtained from borehole studies; deep drillholes drilled in the City of Moscow. Data provided by State Enterprise Geosintez, I. M. Gubkin Center GANG for Complex Analytical Research, and VolgogradNIPIneft.

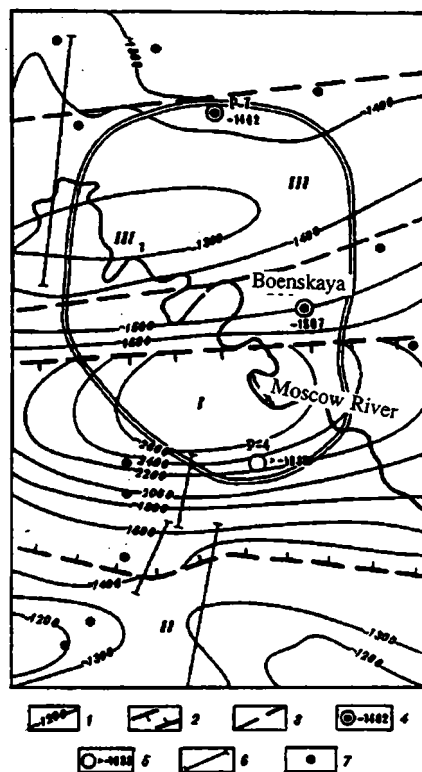


Fig. 1. Map of crystalline basement at Moscow and surrounding area: 1) basement contour, in meters; 2) major tectonic dislocation zones that bound the aulacogen; 3) other dislocation zones; 4) drillholes that penetrate basement (numbers; depth in meters); 5) drillholes that did not penetrate basement (numbers: absolute drillhole depths); 6) seismic profile (KMPB) lines; 7) basement depth, based on TZ KMPV data: I) Moscow Aulacogen; II) Tumsk-Shaturusk Ridge; III) Krasnogorsk Horst; IV) Khimkinsk Uplift.

P-5 and P-7 were deposited in the same manner. In terms of depositional features, rock type and similarly with the Boensk and Shchelkovsk sections, they are correlatable with the Lower Archean Oboyansk Series of the Voronezh Massif.

Based on geophysical data, the Upper Archean basic effusives, schists, and Lower Proterozoic high-magnetic, biotite and amphibolite gneisses of the Moscow Aulacogen occur only locally and represent erosional remnants.

Upper Proterozoic sedimentary rocks overlie crystalline basement rocks across a major unconformity surface. Two complexes, a Riphean and a Vendian occur among them in the aulacogen. Riphean deposits fill the aulacogen. Their distribution area is outlined by the deep flanking faults. The overlying Vendian veneer caps the Upper Proterozoic section. The veneer deposits are widespread in the Moscow Syncline.

Drillholes P-1 and P-4 (south Butovo) penetrated Riphean deposits of the Teplostansk Graben in the 1640-1998 m interval (Fig. 2). Geophysical data indicate that the total thickness of these beds was 900 m. Five cores were taken from drillhole P-4 within the 1640-1813 m interval. Four includes reddish-brown sandstones, with mottling, layers, and lenses of light grayish-rose color and maximum 20 mm thick. Fine-to-medium grained sand medium-to-coarse grained sandstone varieties occur. They included quartz, cemented to different degrees by iron and clay cement, while the bleached zone contained only clayey matter of kaolinitic-illitic composition. Feldspar and quartz-bearing sandstones in the Upper Riphean section did not display bleaching.

In the 1679-1688 m interval the original bedding has been disrupted in the rocks. A contact between various sandstone types occurs along near vertical fractures (Fig. 3) and was traced for a distance of 7 km within core. The contact was

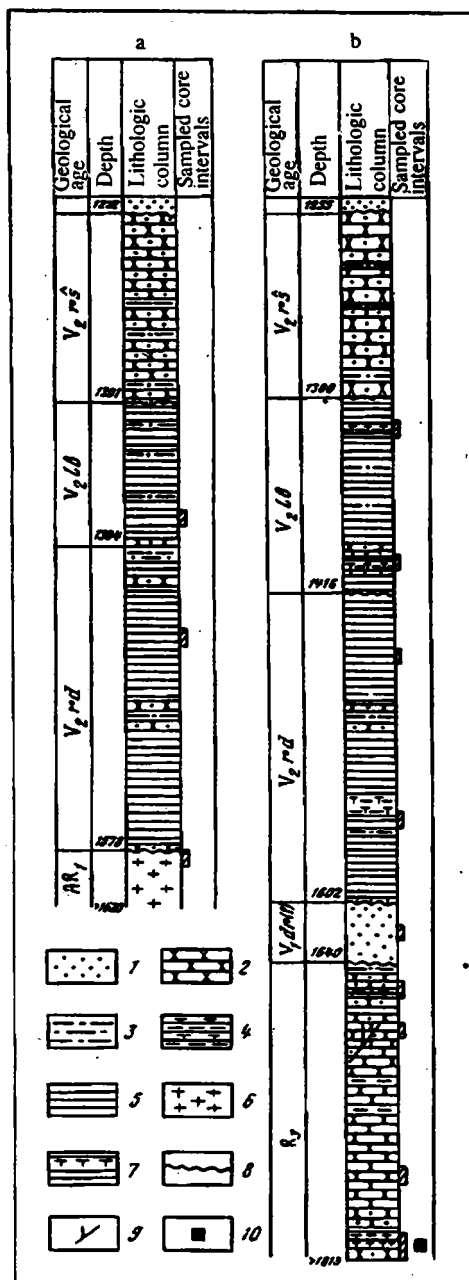


Fig. 2. Geological section of Riphean-Vendian deposits. Drillholes P-7 (a) and P-4 (b): 1) sandy with pebbles and "drenched" clays; 2) sandstones; 3) siltstones; 4) clays, thinly layered ("soaked"), with ash and turf layers; 5) argillites; 6) argillites with pumice ash layers; 7) basic igneous rock; 8) unconformities; 9) lateral break in bedding continuity; 10) oil show. Index: AR₁) Lower Archean; R₃) Upper Riphean; V₁) Lower Vendian (dr-Drevlyansk Series), V₂) Upper Vendian (rd-Redkinsk Subseries); 1b) Lyubimsk Formation (rś- Reshminsk Fm); D₂) Middle Devonian.

straight, slightly undulating, locally branching, completely filled by light-gray kaolinite. The fracture was 1-2 mm wide. Density varied widely, between 10-200 liters/m. Between 1670-1760 m, the drillhole probably traversed a tectonic dislocation zone.

The Riphean sandstones contained only maximum 1% carbonate matter, represented by microgranular siderite and dolomite, generally in the cement. These carbonates were enriched in light ¹²C isotope; the mean $\delta^{13}\text{C}$ content was -23.5‰ .

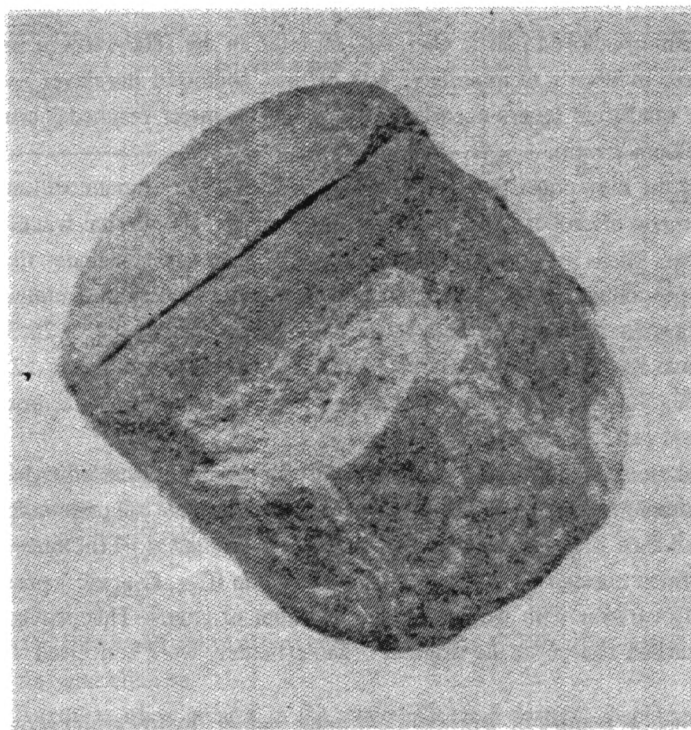


Fig. 3. Sandstone with near vertical fractures (drillhole P-4, 1679-1688 m interval, Upper Riphean).

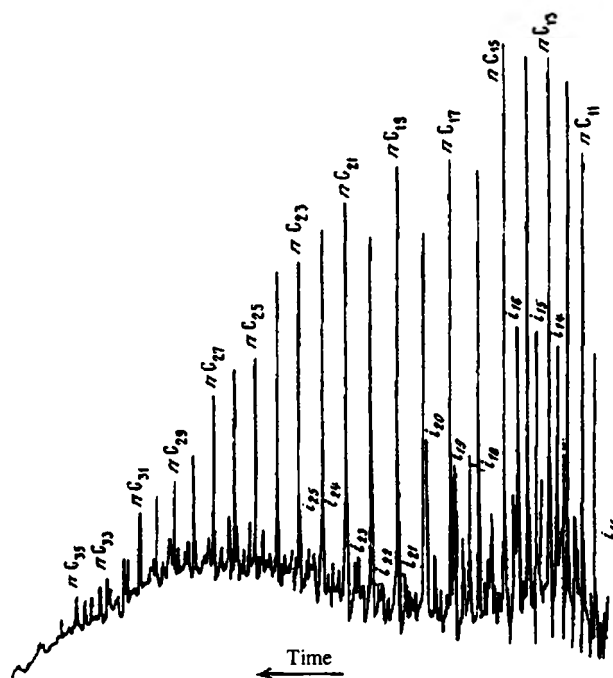


Fig. 4. Hydrocarbon chromatograms from clays in drillhole P-4 (1800-1805 m). Hydrocarbons nC_{11} – nC_{35} -normal paraffinitic, i_{11} – i_{25} -isoprene-bearing.

Insignificant organic concentrations (C_{org}) occurred in the sandstones (maximum 0.18%). The ^{13}C content varied between -26.1 and -27.5% .

A 2-m thick, dark cinnamon-colored plastic clay bed, sampled in the 1800-1805 m interval added gas content to the drilling mud. The clay structure, in Rich's terminology, was of the "contorted intralayer" variety. Maximum 1 mm thick orthotuffite laminae and pebbly sandstone layers occurred. The gravel diameter reached 3 cm. The fresh clay, when freshly broken, gave off a strong petroleum aroma.

X-ray data indicate that the clay consists of 40% kaolinite, 25% illite-montmorillonite mixed-layer minerals, 20% illite and 15% chlorite. The specific micropore surface area was $24 \text{ m}^2/\text{g}$. The detrital fraction is represented essentially by quartz, minor amounts of feldspar, micas and volcanic glass fragments. Carbonates includes microgranular siderite (maximum 1%) of -11.7% carbon isotope content. The clays contained numerous mineralized cinnamon brown film of branching bands and needle shapes. The organic content was high (1.03-1.06%), the $\delta^{13}C$ value, -25.3% .

In the course of chemical and bituminol analyses, the clays correspond to Grade 12 of the luminescence scale. Its bituminoid coefficient was 9.3%. Bituminoids included saturated hydrocarbons (39%), aromatic hydrocarbons (32%), silica gel resins (25%), and asphaltenes (4%).

The chromatogram of bitumoid extract (Fig. 4), obtained from clay, is typical of hydrocarbons derived from sapropel matter that was buried under reducing conditions. This is indicated by the low (0.87) pristane/phytane ratio and predominance of relatively low-molecular n-alkanes over high-molecular ones $\Sigma(nC_{10} - nC_{20})/\Sigma(nC_{21} - nC_{32}) = 1.97$. Normal paraffinitic hydrocarbons with undefined number of carbon atoms in the chain (C_{13} , C_{15} , etc.) predominate among low-molecular alkanes over corresponding hydrocarbons with well established number of atoms. This proves that low-molecular fatty acids in blue-green algae, the main carbon source in the original organic matter, were converted via decomposition by Al-silicate catalysts [3].

In addition of being a general feature of sapropelitic organic matter, hydrocarbon separation from clays characterized organic matter in Precambrian hydrocarbons, in particular Riphean-Vendian deposits of eastern Siberia [5]. This is indicated primarily by the presence of homologous series of relict 12- and 13 monomethyl-replacing alkanes C_{24-30} and their decomposition products, C_{19-24} . These hydrocarbons occur in larger concentrations (17.5%) than normal alkanes of identical molecular size do. These are valid genetic indicators of syngenetic organic matter, studied in the enclosing rocks.

Various opinions persists on the biological origins of 12- and 13- monoethyl-replacing alkanes [5, 7]. The source may have been methyl-replacing acid that, in conjunction with maximum concentrations of C_{24} homologs, was represented by paraffin chains of at least 24 C-atoms. It may also have been cyclopropane-carboxylic acid C_{25} . Al-silicate catalysts may have converted these substances into the relict matter encountered in the samples.

Organic matter, typical of ancient deposits with increased 2 and 3 methylalkane content in particular with C_{15-19} (25.2% of the corresponding n-alkanes), has also been found. It may represent catalytic decomposition products of aliphatic isoacids and anteacids, prevalent in the algal biomass. 7-methylheptadecane, a relict hydrocarbon, probably mixed with 8-methylheptane, occurs in algal methylalkanes [3].

In addition to phytane dominance over pristane in isoprene-bearing hydrocarbons, the pristane/norpristane ratio was low (0.91). High concentrations of trisnorgopane, and low (1.30) adiantane + gopan/transnorgopane ratios characterized polycyclic hydrocarbons. The moretane content was also very low.

Geophysical studies of drillholes P-1 and P-4 indicated the low natural gamma activity (maximum 0.25n A/kg) of the investigated clays. Clays with the highest gamma activity (0.06-0.1n A/kg) values over background formed during the development of Upper Riphean pelitic sedimentary structures. The clay beds here are 1-3 m thick and represent ~15% of the observed section.

The variegated Vendian sequence in the Moscow Aulacogen occurs in the Drevlyansk (?) and Valdai Series. The Vendian deposits are maximum 385 m thick in the Teplostansk Basin and 346 m thick on the north flank of the Krasnogorsk Horst. In the Horst, the Vendian is represented only by the Valdai Series that contains rocks of the Redkinsk and Povarovsk (Lyubimsk and Reshminsk Formations) (Fig. 2).

The Lower Vendian Drevlyansk (?) Series is 40 m thick and of higher clay content than the Riphean beds. The mean natural gamma-activity level of the enclosing rock sequence is 0.4n A/kg; the sand content, ~30%. Drillhole P-4 displayed sands and weakly cemented, light greenish gray sandstones, usually poorly sorted. They contain feldspar and quartz, gritstone layers with quartz pebbles and gravels of maximum 2-3 cm diameter, as well as cinnamon-brown clay layers. Gravels and pebbles were coated with a maximum 1 mm thick, gray carbonate crust, with -17.0% carbon isotope content. Clays in the

TABLE 1. Upper Proterozoic Clay Minerals in Detrital–Clayey Rocks (values in %).

Minerals	Sandstones	Siltstones		Clayey, argillites	
	A	A	B	A	B
Mixed-layer	$\frac{0-4}{2}$	$\frac{0-15}{7}$	35	$\frac{5-25}{18}$	$\frac{15-30}{23}$
Illites	$\frac{3-20}{7}$	$\frac{10-45}{28}$	25	$\frac{20-35}{31}$	$\frac{25-45}{34}$
Kaolinite	$\frac{80-100}{91}$	$\frac{35-85}{58}$	40	$\frac{35-70}{41}$	$\frac{25-52}{41}$
Chlorite	—	$\frac{0-15}{7}$	Traces	$\frac{5-18}{10}$	$\frac{0-5}{2}$

Note: In this and the following table the numerator given the concentration range and the denominator, the arithmetic mean values; A and B – depositional conditions (A – fresh-water; B – marine).

fragments generally were contorted into small folds. They contain kaolinite (70%), illite (30%), minor amounts of montmorillonite–illite mixed-layer minerals, and chlorite.

Quartz, feldspar and aleurolitic mica occurs in the clays. Organic matter, dispersed in the clays was enriched in heavy isotope ^{13}C ($\delta^{13}\text{C} = -25.5\%$).

Similarity between the carbon isotope contents in dolomite that participates in the carbonate crust, in rock fragments of the Drevlyansk Series, and in cement from the underlying Upper Riphean sandstones ($\delta^{13}\text{C} = -17.9\%$) indicates erosion in subsequent pre-Vendian times. Drevlyansk Basin bottom waters intruded at 15-20 m depth. This intrusion introduced heavy isotope ^{13}C .

The Upper Vendian Valdai Series in the Moscow area was laid down on various tectonic structures, separated by distances of maximum 35 km. It is characterized by different section types, of very similar thickness values (Fig. 2); 347 m in drillholes P-1 and P-4 (South Butovo) and 346 m in drillholes P-5 and P-7 (Korovinsk). In both areas the series includes dark gray, horizontally bedded argillites and argillitic clays. They contain microfossils, sapropel films and clumps of organic matter. Kaolinite (40-45%) and illite (30-35%) dominated in the clayey rocks, with minimum amounts of mixed-layer montmorillonite–illite mineral (18-23%) and chlorite (2-10%). The specific micropore surface area range in the clay deposits was 6-16 m²/g.

The Redkinsk and Lyubimsk argillites in drillhole P-4 include thin (maximum 2-3 mm) gray, fine-grained orthotuffite laminae. In both areas aleurolite lenses and layers also occur. Occasional fine and medium-grained sandstones with quartz and feldspars include maximum 5% carbonate matter, represented by dolomite and siderite. The carbon isotope composition of carbonates was varied in these areas. While carbonate minerals of the aleurolite cements in the Redkinsk Subseries in drillhole P-4 contained high concentration of light isotope ^{12}C ($\delta^{13}\text{C} = -21.4\%$), rocks of the same age and type in drillhole P-7 displayed lower ^{12}C isotope values in carbonates and a $\delta^{13}\text{C}$ value of +0.6%. In drillhole P-4, the carbon isotope content of carbonates in Lyubimsk Formation aleurolites, Pavarovsk Subseries, ranged between -6.5 and -10.6%.

In addition, a general sand content increase was indicated in both regions by GIS data in the sections, from the Valdai Series (15-25%) (Redkinsk Subseries) to 50-8% (Reshminsk Fm.). On the north flank of the Krasnogorsk Uplift the sandstone content increased markedly in individual units. Upward in the section the carbon isotope composition in the organic matter was lightened from -26.8-28.0%. The mean organic content of the series was 0.15%.

The Upper Proterozoic sequence under review in one area of the south margin of the Moscow Syncline well characterized deposition conditions. As shown by various authors, aulacogens, in particular the Moscow aulacogen, formed between the Middle and Upper Riphean. Upper Riphean redbeds fill the Teplostansk Graben of the Aulacogen. These formed under arid conditions, in an acidic, low energy, fresh water medium of deposition. The land surface surrounding the Teplostansk Basin was slightly dissected. Therefore, the sediments were essentially fine-grained quartz sands and aleurolites.

TABLE 2. Isotope Composition of Carbonate Minerals and Organic Matter in Upper Proterozoic Rocks

Rocks	Carbon isotope content ^{13}C , ‰			
	carbonates		organic matter	
	A	B	A	B
Sandstones	$\frac{-23,3 + -23,8}{-23,5}$	—	$\frac{-26,1 + -27,5}{-26,7}$	
Aleurolites	$\frac{-10,6 + -21,1}{-15,4}$	+0,6	$\frac{-26,7 + -28,9}{-27,3}$	-30,0
Clays, argillites	-11,7	$\frac{+5,5 + +8,3}{+6,9}$	$\frac{-25,3 + -25,5}{-25,4}$	$\frac{-21,0 + 22,5}{-21,6}$

At the end of the Riphean the region became a slightly undulating plain with underlying graben structures, weakly reflected in the plain's topography.

A significant difference in the mineral composition of clay that includes thin beds and cement of fine detrital rocks (Table 1); the presence of pyroclastic matter in clay beds, gravel and pebble beds, and disseminated organic matter, indicate that they have formed due to explosive volcanic activity. This activity was accompanied by intensive accumulation of pelitic sediments, with abundant organic matter, derived from benthic and planktonic blue-green algae that lived in fresh waters.

The early Vendian Baikal tectogenetic phase in the Teplostansk Graben was best expressed by fine and coarse grained detrital rocks in the Drevlyansk part of the section. The sources of the coarse-grained matter were mainly local uplifts, not basement ridges. Their denudation produced Upper Riphean terrigenous deposits. Erosion interrupted the lateral continuity of the Upper Riphean coal beds and altered them in the sections encountered in drillholes P-1 and P-4.

The south rim of the Moscow Syncline formed in Valdai times. Sandy-clayey sediments of the Redkinsk Subseries accumulated in the Teplostansk Basin and on the north slope of the Krasnogorsk Uplift. The studied portion of the syncline at this time was represented by an at least 50 km wide lowland that included fresh water basins. This coastal plain was level and swampy. It was located above a graben and separated from the epicontinental marine paleobasin by a chain of gently inclined uplifts of the Istrinsk-Kol'chuginsk Ridge.

During a general leveling of the land surface in the region, along with the basin, certain ridge block were also buried in Povarovsk times. This led to southward-directed marine transgression of the paleobasin waters to sediment accumulation and the leveling off of sedimentation rates both in the Teplostansk Basin and on the north slope of the Krasnogorsk Uplift. During Valdai times this was clearly shown by the lithology of the section, the clay mineral composition, the carbon isotope ratios in carbonate minerals, and by species and subspecies spectra of microfossil faunas (M. B. Burzina, personal communication).

The cyclicity of the Povarovsk Subseries sequence, its sand content, and textural-structural rock characteristics indicate (1) rhythmic fluctuations of the epicontinental paleobasin surface, and (2) a gradual increase in hydrothermal activity within its waters at the conclusion of the Upper Proterozoic sediment accumulation phase.

Thus, the geological evolution history of the southern margin of the Moscow Syncline and depositional conditions within its area defined the makeup of sedimentary formations, as well as the nature and subsequent alteration trends of the enclosing rocks and their organic matter content.

In late Riphean times the Teplostansk Graben became filled with mature detrital deposits of quartzitic composition. Less mature feldspar-quartzite varieties formed in late Vendian times. The catagenetic changes were due to quartz corrosion and regeneration, pelitization and leaching of feldspars, biotite, and volcanic glass, as well as chloritization. Kaolinite formed in the fresh-water Teplostansk basin under acidic conditions.

In the catagenetic stage kaolinite was converted into illite and kaolinite. Illite varieties formed in the nearshore zone of the epicontinental paleobasin under almost neutral pH conditions (Table 1). Carbonate minerals of terrigenous rocks, deposited in shallow, fresh basin waters became enriched in light isotope ^{12}C . However monotypic nearshore marine rocks, formed in relatively deeper waters were less enriched in this isotope (Table 2).

Physical–chemical processes prior to present times altered pyroclastic matter, in particular volcanic ash into montmorillonite–illite mixed-layer mineral associations. Different ratios (20-25%) of expanding montmorillonite–illite packets occur in clay minerals of Upper Riphean clay mineral associations and Upper Vendian argillites (maximum 10%). Specific micropore surface ratios (24, respectively, 6-16 m²/g) reflected different degrees of mechanical impact in resulting in increased clay densities. These Riphean and Vendian clay and argillite characteristics were associated with various influences of secondary processes by hydrocarbons that originated from organic rock components.

Starting with molecular composition of organic matter in clays (pristane, $n/C_{17} = 0.32$; phytane $n/C_{18} = 0.45$ and $CPI_{24-32} = 1.04$), the maturity of organic matter is shown to be related to geochemical conditions at the start of catagenesis. Catagenetic processes, initiated by clay minerals, were still quite active then. The catalytic clay impact in the 1800-1805 m interval in drillhole P-4 was calculated by mineral composition as 16.5% at already sufficient high (at least 60°C) temperatures. Their composition indicated the hydrocarbons formed due to significant impact by catalytic reactions. The hydrocarbons derived from clays were very similar to petroleum. This substance was considered having been the ancestor of ancient West Yakutiya oils [2].

In conclusion, lithological–geochemical characteristics of Upper Proterozoic rocks in the south rim of the Moscow Syncline were obtained during the study of drillholes P-4 and P-7. Geophysical studies of drillholes P-1 and P-5 in the city of Moscow indicated the presence of oil and gas prospects in the region. Hydrocarbon prospects exist not only in Vendian but also Riphean complexes. The Teplostansk Graben is in a hydrocarbon-bearing zone where the marginal zones have the best hydrocarbon potential. Zones of prospect include ridges with reverse faults (Moscow Ridge, Vidnovsk Ridge, and other ridges) and the area around drillholes P-1 and P-4, south of Moscow city.

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